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256 VANDERPOOL STREET
NEWARK, NEW JERSEY

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PIGMENT COLOR RESEARCH REPORT

Progress Report

The Phase Rule Study of the System $ZnO-CrO_3-H_2O$ at 25°C

Period Covered: Nov. 1941 - July, 1942.

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Progress Report

Title: The Phase Rule Study of the System $ZnO-CrO_3-H_2O$ at 25°C

Period Covered: Nov. 1941 - July 1942

SUBMITTED BY: R. S. Dong DATE SUBMITTED: Aug.6, 1943

APPROVED BY: R. R. Donnelly 4/27/44 DATE ISSUED: April 28, 1944

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INTRODUCTION:

The following report covering the results of several months work was submitted substantially in its present form in August, 1943. A few minor points were clarified by Dr. Done at the time of his visit to Newark shortly before his death. The only changes which have been made are of an editorial nature.

Obviously, the area of the three component diagram of most interest to us is the one in which the solubility, expressed as concentration of CrO_3 in solution, is relatively low and this region has been explored more completely than the others. In fact, data are lacking at present to enable us to complete the three component phase diagram with certainty; the gaps are indicated in the discussion under "Summary and Conclusions".

R. R. DENSLOW

With the granting to the New Jersey Zinc Company of a patent, U.S.2,251,846[5], on "zinc tetroxychromate" as a new chemical individual and a metal protective pigment, interest in the basic zinc chromates increased greatly. To obtain data on solubility and constitution of basic zinc chromates, this phase rule study of the system ZnO-CrO_3-H_2O was undertaken.

M. Groger[1] made a phase rule study of this system and did not report a "zinc tetroxy chromate". However, his data were very meager in this region and no conclusions as to the existence or non-existence of "zinc tetroxy chromate" $5ZnO.CrO_3.xH_2O$ could be drawn.

In January 1942 a literature survey of the zinc chromates was reported in KM-42-12 (Ref.7). No reference could be found in the literature concerning "zinc tetroxy chromate". Also, no phase rule study other than Groger's was found.

SUMMARY AND CONCLUSIONS:

By a variety of methods (see Experimental Details) mixtures of ZnO, CrO_3 and H_2O were prepared and allowed to come to equilibrium during agitation at constant temperature (25°C.) Subsequent separation of liquid phase and solid phases wet with liquid phase produced samples for analysis. The analytical results are shown in Table I, columns 5, 6, 10 and 11.

The methods of the Phase Rule were applied as described in the section of this report entitled "The Phase Rule Applied to Three Component Systems". It was found that, while several definite compounds were clearly indicated, there was positive evidence of solid solution in the region of solid phase mole ratio of 4.5 to 3.1

and chromate solubility of 0.001 to 6.3% CrO_3. This broad range of chromate solubility includes the region of chromate solubility which, according to our present belief, is desirable for metal protective pigments.

As pointed out in the section on "Phase Rule", additional data in the region of solid solution formation were needed in order to determine the end points (composition of solid phase) of the divergent "tie lines". Therefore, several dry powders were prepared and the analytical results shown in Table II were obtained. No special precautions were taken in drying the samples and it is probable that some were under- and some over-dried. However, an approximation of the composition of the solid phase in the region of solid solution was obtained by plotting in Fig.1 the data of Table II and drawing the best straight line among the points and terminating it at the point of convergence of the next group of tie lines. Because of the low concentration of solute in the liquid phase in the region of solid solution formation, even large inaccuracies in placing the solid phase line result in negligible change in the calculated ZnO : CrO_3 mole ratio in the solid phase.

In Fig.1, the analytical results of Table I, columns 5, 6, 10, 11 and Table II, are plotted on a triangular diagram according to the principles of the Phase Rule. All intersections of tie lines, which points represent solid composition, were calculated by analytic geometry and the results were converted to mole ratios and are shown in Table I, column 12.

From the standpoint of metal protective pigments, the results in the region of less than 1% CrO_3 in the liquid phase were considered of most interest. The triangular graph method is not suited for presenting data for such very dilute solutions, and another procedure was therefore used for plotting the results which greatly magnifies the dilute end of the curve. Shown in Fig. 2 is the graph of the log of the grams of CrO_3 per liter of saturated solution (Table I, col.7) versus the ZnO:CrO_3 mole ratio in the solid phase (Table I, col. 12) Presented also in Fig.2 is the graph of the data (Table VII) taken directly from Groger's paper (1).

Other evidence of the discontinuity in the curve (Fig.2) at mole ratio 4.5 was obtained by preparing a series of mixtures in the region of ratio 4.5 from zinc oxide obtained from different sources. If the displacement of the point of discontinuity from 4.0 (according to Gröger) to 4.5 were due due to presence of a fraction of "unreactive" ZnO, a discontinuity at a different ratio should result for each type of zinc oxide because of probable different fractions of "unreactive" ZnO present. However, using resistance measurements as a measure of composition of the liquid (See Fig.3 for graph of resistance versus composition), mixtures made from either a different lot of Reagent Quality zinc oxide or

the commercial Kadox exhibited a discontinuity at the same $ZnO:CrO_3$ mole ratio of 4.5. The results of these two series of experiments are shown in Tables III and IV and Figs. 4 and 5. The discontinuity at ratio 4.5 was reproduced, also, in conductimetric titrations in which CrO_3 solution was added to ZnO slurry and vice versa.

To present in convenient tabular form the information on the limits of the composition of the various combinations of phases in mutual equilibrium, Table V was compiled from Figures 1 and 2.

The results of microscopic examination of the crystals in equilibrium mixtures are shown in Table VI. Groger[1] obtained the same type of crystals at mole ratio 4 and 3 as were obtained in this study in the range of solid solution. The 2:1 crystals he described as "cloudy, spherical crystallites", which description fits the 2:1 product found in the present study. He described the 1:1 compound as "small crystals", which also corresponds qualitatively with observations made in the present study.

The following conclusions may be drawn regarding the system at 25°C.

1. "Zinc tetroxy chromate" as described in U.S.2,251,846 does not exist. A solid phase containing more than 4.5 moles ZnO to 1 mole CrO_3 is a mixture of zinc oxide and the limiting solid solution 4.5 $ZnO:CrO_3$. (Note: X-Ray diffraction studies made by the Experimental Station on a pigment with the empirical composition 5 $ZnO:CrO_3$ showed the pattern of free zinc oxide as well as the ZnO-free pattern of the 4.5 $ZnO:CrO_3$ pigment. The latter pattern corresponded with the pattern presented by the N.J. Zinc Co. in the patent on "Zinc tetroxy chromate".)

2. "Zinc trioxy" (4 $ZnO.CrO_3$) and "zinc dioxy chromate" (3 $ZnO.CrO_3$) both reported by Groger[1], do not exist as definite chemical compounds. Instead, a series of solid solutions varying in composition between the limits of $ZnO:CrO_3$ mole ratio of 4.5 to 3.1 exists. (Note: X-Ray diffraction studies by the Experimental Station showed that several lines of the 4.5 pattern disappear to form the 3.1 pattern. This is a phenomenon of crystalline solid solutions.) (Groger[1] described both the 4:1 and 3:1 compounds as identical under the microscope.) The wide range (6,000-fold change) of chromate solubility of the solid solution allows the preparation of a pigment with a chromate solubility anywhere in this range. Although the points in the region of solid solution show some tendency toward scattering (See Fig.2) it is believed that a standardized method of manufacture would be reproducible. It is believed that equilibrium between the solution and the surface of crystals of solid solution is established readily, but that constancy of composition throughout the length, breadth, and thickness of a crystal is approached slowly, as the rate of diffusion of atomic groups inside a crystal is naturally limited. One possible disadvantage to the use of this type of material as a

metal protective pigment should be mentioned; namely, the amount of CrO_3 available is quite limited and its solubility is reduced quite rapidly by leaching. However, leaching merely produces the same combination of ingredients as is present in "zinc tetroxy chromate", which itself has shown promise as a metal protective pigment in tests conducted by the New Jersey Zinc Company.

3. The compounds $2ZnO.CrO_3.2H_2O$ and $ZnO.CrO_3.2H_2O$ are clearly indicated. However, the nature of the solid phase of composition between the two is not clear. The existence of a 1.5 $ZnO:CrO_3$ compound (reported by Groger) is neither confirmed nor disproved. (Note: X-Ray diffraction studies made by the Experimental Station showed dry material with a $ZnO:CrO_3$ ratio of 2.5 to have the pattern of the 3.1 limiting solid solution and of a 2:1 compound. Examination of 1:1 material showed a different pattern.) (Note: The compounds $2ZnO.CrO_3.1.5\ H_2O$ and $ZnO.CrO_3.H_2O$ reported by Groger[1] are believed to have been the result of his over-drying of the 2:1:2 and 1:1:2 compounds of the liquid-solid equilibrium mixtures. (The dry powders of mole ratio 2.57 and 2.25 (No.5 and 6, Table I) were definitely overdried, as indicated by their positions in Fig.1.)

4. The dotted-line portion of the liquid curve (Fig.1) is the only portion which remains uncertain. It is believed that along this line lies the varying liquid compositions which are in equilibrium with zinc dichromate. (Note: Hoffmann[6] reported the compounds $ZnO.2CrO_3$ and $ZnO.2CrO_3.3H_2O$)

5. The compound $ZnO.CrO_3.3H_2O$ reported by Hoffmann[6] is clearly indicated by this phase rule study.

6. The compound CrO_3 is clearly indicated as being the solid phase associated with the final segment of the liquid curve.

THE PHASE RULE APPLIED TO THREE COMPONENT SYSTEMS

(For the purpose of illustration Figure 7 is presented)

The Phase Rule is applicable only to systems all phases of which are mutually at physical and chemical equilibrium. Mathematically, the Phase Rule is stated as

$$F = C - P + 2 \qquad \text{(Eq. 1)}$$

where F is the number of degrees of freedom (independent variables, such as temperature, pressure, composition of a phase, which may be varied without the appearance of disappearance of a phase); where C is the number of components (smallest number of chemical species which may be used

to express the composition of each phase of the system); where P is the number of phases present (one gaseous, one or more liquid, and one or more solid).

Let us consider a three component system consisting of H_2O and solid compounds A and B. In the presence of the atmosphere, air is a 4th component, but pressure of the system is maintained constant at one atmosphere and is thus eliminated as a variable. Thus, at constant pressure

$$F = (C - P + 2) - 1 = 4 - P + 2 - 1 = 5 - P \quad \text{(Eq. 2)}$$

At constant pressure and temperature

$$F = (5 - P) - 1 = 4 - P \quad \text{(Eq. 3)}$$

From equation 3 it may be calculated that presence of two solid phases, one liquid phase, and one vapor phase (at constant pressure and temperature) allows zero degrees of freedom. Therefore each of the four phases must maintain constant composition or one of the phases must disappear. The compositions of such invariant mixtures lie in areas 2 I II, 3 III IV, 4 IV V (Fig. 1).

Mixtures containing one solid phase and, therefore, possessing one degree of freedom lie in areas I 12, II III 32, IV 34, V 45. The independent variable is the percentage of one of the components in the liquid phase; the other components are altered dependently in such a manner that the liquid compositions lie on the line 12345.

In the area above line 12345 there is no solid phase present and a mixture there has two degrees of freedom, namely, the percentage composition of two of the components in the liquid.

Experimentally, a Phase Rule graph of a real system is worked out by analysing the liquid phase of an equilibrium mixture and analysing a mixture of liquid and solid phases. Greater accuracy in graphing is obtained by removing as much liquid as possible before analysing the mixture. The anlytical results for each mixture are represented on the triangular composition diagram by a pair of points. The straight line thru the two points, when extended toward the region of less liquid content will pass through the composition of the solid phases. Intersection of two or more tie lines from different liquid compositions in a single point determines the chemical composition of a compound, which constitutes the solid phase. Points I, IV, and V represent such compounds. (Ref.9).

Tie lines emanating from a point representing a single liquid composition lead to a solid phase composition consisting of a mixture of two phases. Such liquid compositions are the points 2, 3, and 4. Since points IV and V represent chemical

compounds, the tie lines from point 4 terminate in a straight line connecting points IV and V, which line represents mixtures of compounds IV and V in various proportions.

However, complications arise for this "method of intersections" in regions of varying liquid composition where the tie lines do not intersect in a point. Such a region is line 23, which represents a series of liquid solutions in equilibrium with a series of "solid solutions". It is impossible to determine the composition of the solid phases without securing additional data. Ingenious means of obtaining samples of the solid phases free of all liquid and without decomposition must be devised, and the samples analysed. Thus the line I II III IV may be constructed. The points II and III are the limiting compositions in the series of solid solutions. The straight segment I II represents mixtures of compound I and limiting solid solution II. The straight segment III IV represents mixtures of limiting solid solution III and compound IV. (For further discussion of this method of indirect analysis in relation to solid solution formation see Bancroft, Ref. 8)

EXPERIMENTAL DETAILS

Methods of Preparation

Usually, mixtures containing three to five grams of solid phase per 100 cc were prepared. The following outline describes the various methods of preparation. Distilled water, Reagent quality ZnO (dry process) and Reagent quality CrO_3 were used and mixed during constant agitation.

A. To a prepared slurry of zinc oxide, chromium trioxide solution was added.

B. To a saturated solution of ZnO and CrO_3 zinc oxide slurry was added.

C. To a mixture prepared by Method A zinc oxide slurry was added.

D. To a mixture prepared by Method A water was added.

E. To a zinc oxide slurry a saturated solution of ZnO and CrO_3 was added.

F. Zinc oxide slurry was added to CrO_3 solution.

G. Solid CrO_3 was added to a saturated ZnO, CrO_3 solution.

H. Saturated solution of Zno and CrO_3 was evaporated in a desiccator over CaCl2 or P_2O_5. The resulting mixture was ground smooth in a mortar.

J. Supersaturated solutions were prepared by adding zinc oxide (slurried or dry) to saturated solutions of ZnO and CrO_3. After stirring a few minutes the mixture was filtered. Upon standing for various lengths of time a precipitate usually formed. Excess liquid was decanted off and the resulting mixture was used.

K. Supersaturated solution was prepared by filtering a ZnO-CrO_3-H_2O mixture at 0-3°C. Upon warming, precipitate usually formed. Excess liquid was decanted off.

L. A large quantity of an equilibrium mixture of $2ZnO \cdot CrO_3 \cdot 2H_2O$ and its saturated solution 5.2% ZnO, 12.2% CrO_3 was vat washed 16 times. From time to time during the washing process a sample of the settled mixture was removed and placed in a shaking flask for attainment of equilibrium at 25°C.

Each mixture was placed in an Erlenmeyer flask of 125 c.c. capacity (500 c.c. size for some of the less soluble mixtures). The flasks were fitted with ground-in glass stoppers lubricated with a small amount of inert grease and securely held in place while in the shaking apparatus in the thermostat by pressure from a half-inch thickness of sponge rubber.

Agitation of the mixtures while attaining equilibrium was provided by means of a "ferris wheel" type of shaking apparatus with spaces for 24 flasks. This was purchased from the Arthur H. Thomas Co. (Catalog Item No. 8910) and was operated in a water bath whose temperature was held at 25 ± 0.01°C. by means of a toluene-mercury thermoregulator and a vacuum tube relay controlling and immersion heater.

Changes in concentration of solutes in the mixtures while approaching equilibrium were conveniently followed by measuring the resistance of a dip-in conductance cell placed directly in the reaction mixtures from time to time.

After equilibrium conditions were believed to have been reached the liquid phase was separated at constant temperature and without evaporation by allowing the mixture to drain by gravity through the fritted glass plug of a Pyrex filtering crucible. A small beaker served to collect the filtrate, and both filter and beaker were contained in a wide-mouth glass bottle tightly capped and submerged in the water bath during filtration.

For analysis, a sample of the liquid was transferred to a weighing bottle by means of a pipette of suitable size. Usually the volume in the pipette was adjusted to the mark, and a measure of the density was thereby obtained. However, these density results are inaccurate to the extent of "drainage error" in transferring the more dense and viscous liquids. Densities obtained in this manner are shown in Table I and Fig. 6.

After the liquid had drained from it, the resulting paste was prepared for analysis in one of the following ways.

A. A sample was transferred to a weighing bottle.

B. A sample of paste was placed between pieces of porous porcelain plate in a closed bottle at 25°C for further removal of mother liquor. A sample of the thickened paste was transferred to a weighing bottle.

C. The filter containing the paste was removed from the thermostatted bottle and was quickly subjected to vacuum filtration only to the extent that no air passed through the filter. A sample of the thickened paste was then transferred to a weighing bottle.

After being weighed, the samples of liquid and of paste were transferred to volumetric flasks. A few drops of dilute sulfuric acid were used to dissolve the paste. Water was added to bring to proper volume and aliquot portions of suitable size were taken for zinc and chromate analyses.

Chromate was determined by the iodometric method for zinc yellow described in KCR #46.

Unsatisfactory results were obtained by the H_2S method for zinc in zinc yellow. Consequently, a method for zinc was developed especially for this study. Standard methods (2,3,4) using 8-hydroxy quinoline as a quantitative precipitant for zinc were modified. Ammonium hydroxide and ammonium chloride were employed, producing an alkaline solution to prevent the reduction of the CrO_4 radical by the organic reagent and producing a solution of complex zinc salt to prevent precipitation of basic zinc compounds until addition of the reagent. This method was subsequently set up as KCR 133.

Water was determined by the method described in KCR 46.

Methods of Calculating the Solid Phase End of the Tie Lines. (These calculated points are shown in Table I, column 12.)

A - The compositions of the dry powders shown in Table II were plotted on Fig.1. The best straight line was drawn through the point K ($2ZnO \cdot CrO_3 \cdot 2H_2O$) and among the experimental points. It is emphasized that this resulting line represents only an approximation of the course of the solid phase composition. Actually, at mole ratio 3.1 a "break" in the solid phase curve may be expected. The intersection of this line with the straight tie-line determined by the pair of liquid and paste points was calculated by Analytic Geometry. This involved using the % ZnO as the x-coordinate and the % CrO_3 as the

y-coordinate and thus obtaining an equation for the line through any pair of points. The Analytic formula $\frac{y - y_1}{X - X_1} = \frac{y_2 - y_1}{X_2 - X_1}$

was used. Here substript 1 represents one point and subscript 2 represents the other point of the pair. For example the equation for the line through points (10% ZnO, 20% CrO_3) and (16% ZnO, 22% CrO_3) would be $\frac{Y - 10}{X - 20} = \frac{6}{2}$

By solving two such equations simultaneously for X and y the coordinates of their point of intersection are obtained with an accuracy unobtainable with a graphical method.

B - As an arbitrary line upon which to calculate intersections with tie lines converging toward $ZnO \cdot CrO_3 \cdot 2H_2O$ the straight line passing through the compositions CrO_3 and $ZnO \cdot CrO_3 \cdot 2H_2O$ was chosen. Intersections were calculated by Analytic Geometry.

C - As the line upon which to calculate intersections of tie lines in the vicinity of $ZnO \cdot 3CrO_3 \cdot 3H_2O$, the line passing through $ZnO \cdot 3CrO_3 \cdot 3H_2O$ and CrO_3 was chosen.

D - The intersection of the tie line with the ZnO-free axis was calculated.

From the data of Table I, Fig. 6 was constructed in order to obtain, by interpolation, the densities of solutions which were not determined directly.

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TABLE I

ANALYTICAL RESULTS ON LIQUID PHASE AND PASTE AND CALCULATIONS FROM THEM

1	2	3	4	5	6	7	8	9	10	11	12	13
			LIQUID PHASE						PASTE		SOLID PHASE	
Designation of Mixture	Time Agitated at 25°C (Days)	Resistance of Mixture (OHMS)	Density gm/ml	ZnO %	CrO_3 %	CrO_3 gm/l	Mole Ratio ZnO/CrO_3	Method of Separation from liq.	% ZnO	% CrO_3	Mole Proportion ZnO:Cr_2O_3:H_2O	Method of Calculation
			MIXTURES PREPARED BY METHOD A									
		(3.53)			(3.09)	(2.09)						
316 Y	31	3420 (3.48)	-	.0818	.0012 (3.170)	.012 (2.18)	1.0	C	1.11	0.137	10 : 1 : ?	-
213 Y	17	3010 (3.42)	-	.00892	.00148 (3.262)	.015 (2.25)	.76	A	4.36	1.106	4.85 : 1 : 3.90	A
217 S	16	2630 (3.318)	-	.00824	.00183 (3.431)	.018 (2.43)	.83	A	3.94	1.073	4.52 : 1 : 3.68	A
316 S	17	2080 (2.27)	-	.00205	.00270 (2.732)	.0270 (1.73)	.93	B	9.78	2.690	4.44 : 1 : 3.62	A
1229 T	44	185 (1.636)	0.997	.031	.0539 (1.518)	0.54 (0.517)	.706	A	5.13	1.592	4.17 : 1 : 3.45	A
408 D	7	43.3 (1.976)	-	.1824	.3293 (1.518)	3.29 (0.517)	.682	C	10.905	3.868	3.67 : 1 : 3.12	A
302 T	17	37.7 (1.638)	1.000	.1812	.3294 (1.534)	3.29 (0.534)	.676	B	36.80	10.65	4.29 : 1 :3.53	A
408 X	1/2	43.5 (1.600)	-	.1894	.3419 (1.561)	3.419 (0.560)	.680	C	11.83	4.225	3.64 : 1 : 3.09	A
408 M	7	39.8 (1.571)	-	.1970	.3636 (1.603)	3.636 (0.604)	.665	C	11.83	4.825	3.65 : 1 : 3.10	A
408 E	7	37.2 (1.479)	-	.2199	.4014 (1.669)	4.018 (0.670)	.672	C	11.87	4.168	3.68 : 1 : 3.12	A
213 K	6	30.18 (1.487)	1.002	.250	.467 (1.727)	4.68 (0.727)	.657	A	6.86	2.393	3.78 : 1 : 3.19	A
410 F	10	30.7 (1.248)	-	.282	.533 (1.967)	5.34 (0.970)	.650	C	10.25	3.94	3.52 : 1 : 3.02	A
213 R	6	17.72 (1.116)	1.008	.4705	.926 (0.140)	9.33 (1.146)	.624	A	6.66	2.951	3.62 : 1 : 3.08	A
213 N	6	13.85 (1.040)	1.014	.682	1.382 (0.270)	14.0 (1.279)	.606	A	7.02	3.517	3.46 : 1 : 2.98	A
216 N	11	10.96 (.863)	1.020	.902	1.862 (0.374)	19.0 (1.386)	.595	A	7.25	3.996	3.40 : 1 : 2.93	A
302 J	1	7.3	1.027	1.148	2.363	24.3	.597	A	5.88	4.005	3.26 : 1 : 2.84	A

1	2	3	4	5	6	7	8	9	10	11	12	13
			LIQUID PHASE					PASTE			SOLID PHASE	
Designation of Mixture	Time Agitated at 25°C (Days)	Resistance of Mixture (OHMS)	Density gm/ml	ZnO %	CrO_3 %	CrO_3 gm/l	Mole Ratio ZnO/CrO_3	Method of Separation from liq.	% ZnO	% CrO_3	Mole Proportion ZnO:CrO_3:H_2O	Method of Calculation
					MIXTURES PREPARED BY METHOD A (cont'd)							
		(.881)			(0.434)	(1.447)						
313 H	10	7.6	1.031	1.267	2.715	28.0	.573	A	7.185	4.650	3.39 : 1:2.93	A
"	"	"	"	"	"	"	"	B	22.06	9.55	3.37 : 1:2.92	"
		(.699)			(0.606)	(1.627)						
302 H	1	5.8	1.049	1.904	4.040	42.4	.579	A	7.47	5.89	3.17 : 1:2.78	A
		(.647)			(0.676)	(1.700)						
313 J	7	4.65	1.057	2.157	4.742	50.10	.558	B	18.73	9.94	3.25 : 1:2.83	A
		(.602)			(0.756)	(1.785)						
216 D	11	4.0	1.070	2.575	5.705	61.0	.554	A	6.105	7.415	2.18 : 1:2.12	A
		(.486)			(0.804)	(1.837)						
313 I	10	3.06	1.078	2.830	6.376	68.7	.545	A	10.235	10.015	2.11 : 1:2.07	A
"	"	"	"	"	"	"	"	B	28.22	18.8	2.10 : 1:2.07	A
		(.556)			(0.817)	(1.851)						
305 I	1	3.6	1.081	2.986	6.56	70.9	.559	A	8.655	8.232	3.20 : 1:2.80	A
		(.398)			(0.900)	(1.941)						
302 S	1	2.5	1.099	3.564	7.938	87.3	.551	A	11.75	11.96	2.03 : 1:2.02	A
		(.324)			(1.101)	(2.168)						
126 S	15	2.11	1.167	5.385	12.625	147.1	.524	A	10.69	14.87	2.006 :1:2.004	A
		(.137)			(1.296)	(2.404)						
126 S	12	1.37	1.283	8.27	19.77	253.5	.514	A	20.20	23.26	2.013 :1:2.007	A
		(.124)			(1.316)	(2.431)						
126 X	15	1.33	1.299	8.65	20.73	270	.513	A	18.69	23.48	2.013 :1:2.008	A
					(1.378)	(2.512)						
330 N	1	-	1.361	9.94	23.88	325	.511	B	25.87	27.24	2.015 :1:2.010	A
423 S	1	-	-	19.45	48.73	-	.490	A	-	-	-	-
					MIXTURES PREPARED BY METHOD B							
		(.107)			(1.315)	(2.430)						
218 U	1	1.28	1.301	8.66	20.65	269	.515	A	13.68	22.03	2.016 : 1:2.011	A
		(.190)			(1.505)	(2.692)						
302 N	3	1.55	1.536	13.19	32.03	492	.506	A	20.09	32.54	1.86 : 1 : 1.91	A
						(2.750)						
608 F	21	-	-	14.21	35.20	563	.496	C	26.45	35.50	1.78 : 1 : 1.86	A
		(.290)			(1.566)	(2.784)						
218 S	1	1.95	1.656	15.06	36.78	608	.503	A	22.95	38.23	1.26 : 1 : 2.52	B

1	2	3	4	5	6	7	8	9	10	11	12	13
Desig-nation of Mixture	Time Agitated at 25°C (Days)	Resist-ance of Mixture (OHMS)	LIQUID PHASE					PASTE			SOLID PHASE	
			Density gm/ml	ZnO %	CrO_3 %	CrO_3 gm/l	Mole Ratio ZnO/CrO_3	Method of Sep-aration from liq.	% ZnO	% CrO_3	Mole Proportion $ZnO:CrO_3:H_2O$	Method of Calcu-lation
MIXTURES PREPARED BY METHOD B (cont'd)												
		(.405)			(1.596)	(2.834)						
306 H	4	2.54	1.729	16.14	39.47	682.	.502	A	20.65	40.54	1.09 : 1 : 2.18	B
		(.415)			(1.593)	(2.828)						
218 J	1	2.6	1.721	15.95	39.20	674	.500	A	23.62	41.75	.985 : 1 : 1.97	B
		(.663)			(1.614)	(2.864)						
316 G	2	4.6	1.781	16.78	41.11	731	.501	B	35.48	45.61	.998 : 1 :2.00	B
		(.939)			(1.649)	(2.925)						
316 K	2	8.7	1.891	18.09	44.54	841	.499	B	28.62	45.92	.961 : 1 : 1.92	B
		(1.217)			(1.670)	(2.964)						
316 B	2	16.5	1.972	18.95	46.74	921.	.498	B	35.51	47.16	.956 : 1 : 1.91	B
MIXTURES PREPARED BY METHOD C												
		(.756)			(0.547)	(1.565)						
302 D	8	5.7	1.041	1.625	3.523	36.7	.567	A	8.18	5.593	3.36 : 1 : 2.91	A
MIXTURES PREPARED BY METHOD D												
		(.756)			(I.348)	(0.348)						
409 W	81	57	-	.125	.223	2.23	.690	C	12.62	4.40	3.64 : 1 : 3.09	A
		(1.736)			(I.384)	(0.384)						
409 T	7	54.4	-	.1340	.2420	2.42	.680	C	11.22	3.878	3.72 : 1 : 3.15	A
		(.643)			(0.656)	(1.678)						
306 F	5	4.4	1.054	2.061	4.527	47.7	.559	A	7.660	5.966	3.87 : 1 : 3.25	A
		(.447)			(0.803)	(1.835)						
302 U	1	2.8	1.078	2.813	6.353	68.4	.544	A	11.325	10.48	2.14 : 1 : 2.10	A
		(.114)			(1.432)	(2.587)						
302 R	3	1.30	1.425	11.23	27.06	386	.510	A	17.89	28.22	1.91 : 1 : 1.94	A
424 C	5	-	2.093	18.55	54.37	-	.419	A	-	-	-	
MIXTURES PREPARED BY METHOD E												
		(2.017)			(I.045)	(0.045)						
410 S	10	104	-	.0658	.111	1.11	.73	C	12.36	3.90	3.98 : 1 : 3.32	A
		(1.813)			(I.318)	(0.318)						
410 C	10	65	-	.116	.208	2.08	.685	C	10.13	3.40	3.81 : 1 : 3.21	A
		(0.919)			(0.404)	(1.417)						
421 X	9	8.30	1.029	1.187	2.538	26.11	.575	C	10.815	5.656	3.43 : 1 : 2.86	A
		(.765)			(0.579)	(1.600)						
421 T	9	5.82	1.046	1.745	3.798	39.64	.565	C	10.88	6.675	3.36 : 1 : 2.91	A

1	2	3	4	5	6	7	8	9	10	11	12	13
			LIQUID PHASE					PASTE			SOLID PHASE	
Designation of Mixture	Time Agitated at 25°C (Days)	Resistance of Mixture (OHMS)	Density gm/ml	ZnO %	CrO_3 %	CrO_3 gm/l	Mole Ratio ZnO/CrO_3	Method of Separation from liq.	% ZnO	% CrO_3	Mole Proportion ZnO:CrO_3:H_2O	Method of Calculation
		(.720)			(0.637)	(1.660)						
421 D	9	5.25 (.6513)	1.055	1.969	4.331 (0.731)	45.69 (1.759)	.558	C	11.49	7.220	3.48:1:2.94	A
421 R	9	4.48	1.066	2.431	5.388	57.42	.553	C	11.49	8.810	3.42:1:3.95	A
					MIXTURES PREPARED BY METHOD F							
		(1.648)			(1.540)	(0.540)						
408 J	7	44.5	-	.1840	.3470	3.467	.651	C	12.52	4.412	3.67:1:3.12	A
					MIXTURES PREPARED BY METHOD G							
424 S	5	-	1.987	12.68	59.67	1185	.260	A	-	-	-	
					MIXTURES PREPARED BY METHOD H							
			M			(3.041)						
529 O	7	-	2.1522	20.38	51.01	1098	.490	A	23.50	53.32	1:1.69:2	C
505 T	14	-	-	18.72	52.74	-	.436	C	18.65	61.90	1:3.02:3	C
505 J	4	-	-	17.96	53.40	-	.413	C	18.73	64.80	1:2.98:3	C
529 E	21	-	-	12.44	60.53	- (3.057)	.253	C	16.97	68.06	1:3.15:3	C
505 E	18	-	1.890	9.07	60.20	1140	.185	C	1.79	91.8	0 : 1 : 0.024	D
					MIXTURES PREPARED BY METHOD J							
						(0.512)						
506 Q	7	-	1.000	.1802	.3250	3.250 (0.789)	.681	C	18.07	5.90	3.89:1:3.26	A
526 F	7	-	1.004	0.321	0.613	6.15 (1.010)	.643	A	1.478	0.974	3.84:1:3.23	A
506 X	7	-	1.009	.5127	1.017	10.26 (1.601)	.620	C	15.51	6.35	3.33:1:2.89	A
506 R	6	-	1.046	1.747	3.816	39.90 (1.688)	.562	C	9.47	6.45	3.125:1:2.75	A
526 E	7	-	M 1.0539	2.105	4.631	48.8 (1.810)	.558	A	6.53	6.745	2.27:1:2.18	A
506 D	6	-	1.074	2.715	6.014	64.6	.553	C	27.80	18.98	2.045:1:2.03	A

MIXTURES PREPARED BY METHOD J (cont'd)

1	2	3	4	5	6	7	8	9	10	11	12	13
			LIQUID PHASE					PASTE			SOLID PHASE	
Designation of Mixture	Time Agitated at 25°C (Days)	Resistance of Mixture (OHMS)	Density gm/ml	ZnO %	CrO_3 %	CrO_3 gm/l	Mole Ratio ZnO/CrO_3	Method of Separation from Liq.	% ZnO	% CrO_3	Mole Proportion H_2O:CrO_3:ZnO	Method of Calculation
						(2.200)						
507 F	6	-	-	5.71	13.42	158.5	.523	C	31.65	23.99	2.011:1:2.007	A
						(2.623)						
506 N	11	-	1.461	11.81	28.74	419.9	.505	C	22.06	29.98	2.006:1:2.005	A
						(2.695)						
522 P	12	-	1.540	13.28	32.18	495	.506	A	22.74	32.82	1.87:1:1.92	A
						(2.853)						
507 F	6	-	-	16.48	40.49	713	.500	C	29.18	44.83	0.95:1:1.92	B
					MIXTURES PREPARED BY METHOD K							
		(2.1461)			(.792)	(1.796)						
521 D	8	140	-	0.039	0.062	.625	.77	C	15.57	4.72	4.09:1:3.39	A
					MIXTURES PREPARED BY METHOD L							
		(3.0)			(3.699)	(2.70)						
417 V	30	1000	-	.0043	.0050	0.05	.95	-	1.016	.808	4.19:1:3.46	A
		(1.913)			(1.100)	(0.699)						
417 N	13	81.8	-	.0746	0.1258	1.256	.730	A	10.34	3.306	3.945:1:3.30	A
		(1.380)			(1.783)	(0.785)						
416 P	7	24.8	-	0.3147	0.607	6.095	.636	B	39.92	14.18	3.51:1:3.00	A
		(1.083)			(0.164)	(1.171)						
416 J	7	12.1	-	0.715	1.459	14.81	.603	B	31.90	17.37	2.32:1:2.22	A
		(.857)			(0.410)	(1.423)						
416 E	7	7.2	-	1.203	2.571	26.48	.575	B	31.51	19.45	2.08:1:2.06	A
		(.760)			(0.503)	(1.519)						
416 A	7	5.75	-	1.480	3.187	33.05	.570	B	30.04	19.05	2.055:1:2.04	A
					MIXTURE PREPARED FROM CrO_3 AND H_2O							
						(3.029)						
505 S	23	-	1.700	0	62.95	1070	0.0	-	-	-	0 : 1 : 0	-

NOTE: A number in parentheses is the logarithm of the number under it.

x These values of density were determined in a 25 cc. pycnometer at 25.0°C and were converted to vacuo.

TABLE II

ANALYSES OF DRY POWDERS (VALUES IN PARENTHESES OBTAINED BY DIFFERENCE)

No.	Designation	COMPOSITION ZnO %	Cr_2O_3 %	H_2O %	MOLE RATIO $ZnO:Cr_2O_3:H_2O$	REMARKS References are to Table I
1	302 TD	67.3	20.05	12.65	4.12:1:3.50	Paste of 302T. Pressed between porous plates. Dried 3 days at 140°F.
2	410 SD	66.2	20.9	12.92	3.89:1:3.43	Paste of 410S. Dried at room temperature over calcium chloride. Drying believed to be incomplete due to large amount of water absorbed by the desiccant.
3	409 TD	64.2	22.4	13.37	3.52:1:3.31	Paste of 409T. Dried at room temp. over calcium chloride. Drying believed to be incomplete due to large amount of water absorbed by desiccant.
4	410 FD	63.7	24.5	11.80	3.19:1:2.67	Paste of 410F. Dried in air at room temp. to 12.8% H_2O. Drying completed over fresh calcium chloride desiccant.
5	313 ED	60.66	28.88	(10.8)	2.57:1:2.07	Paste of 313E sucked dry as possible by filtration. Filter cake allowed to dry at 140°F for 3 days.
6	313 JD	58.26	31.74	(10.0)	2.25:1:1.75	Paste of 313J pressed between porous plates. Dried one day at 140°F.
7	927-46A	66.91	20.47	(12.6)	4.01:1:3.31	CrO_3 solution added to Kadox slurry. Filtered on Buchner funnel. Dried overnight at 140°F.
8	927-46B	69.05	17.16	(13.8)	4.94:1:4.46	
9	927-TNB	67.3	20.77	(13.0)	3.98:1:3.47	CrO_3 solution added to slurry of Reagent ZnO. Filtered on Buchner funnel. Dried overnight at 140°F.

TABLE III

RESISTANCE MEASUREMENTS OF A SERIES OF MIXTURES MADE BY ADDING VARYING AMOUNTS OF CrO_3 SOLUTION TO A CONSTANT AMOUNT OF A SLURRY OF C.P. BAKER'S ANALYSED ZnO. (AFTER 3 DAYS AGITATION AT 25°C.)

	COMPOSITION OF MIXTURE			RESISTANCE ***	
	gm ZnO*	gm.CrO_3**	ZnO:CrO_3 mole ratio	ohms	(log)
1128 A	1.357	0.265	6.3	5000	(3.70)
1128 B	"	.273	6.1	5130	(3.71)
1128 C	"	.283	5.9	5180	(3.71)
1128 D	"	.309	5.4	5160	(3.71)
1128 F	"	.321	5.2	5200	(3.72)
1128 E	"	.327	5.1	5080	(3.71)
1128 G	"	.333	5.0	5000	(3.70)
1128 H	"	.341	4.9	5090	(3.71)
1128 I	"	.355	4.7	4840	(3.69)
1128 J	"	.379	4.4	3600	(3.56)
1128 K	"	.397	4.2	1150	(3.06)
1128 L	"	.407	4.1	680	(2.83)
1128 M	"	.417	4.0	480	(2.68)
1128 N	"	.427	3.9	350	(2.55)
1128 O	"	.450	3.7	207	(2.32)

* Added as a slurry 2.714 gm ZnO per 100 ml.

** Added as 7% solution of CrO_3.

*** Measured by pouring the mixture into a small conductivity cell.

TABLE IV

RESISTANCE MEASUREMENTS OF A SERIES OF MIXTURES MADE FROM A SLURRY OF KADOX ZnO AND SOLUTION OF CrO_3. (AFTER 3 DAYS AGITATION AT 25°C.)

Designation	MIXTURE COMPOSITION * Moles ZnO per 100 gm.	Moles CrO_3 per 100 gm.	ZnO:CrO_3 Mole ratio	RESISTANCE ** ohms	(log)
1231 A	.0459	.00804	5.71	3300	(3.52)
1231 B	.0452	.00869	5.20	3330	(3.52)
1231 C	.0445	.00925	4.80	3260	(3.51)
1231 D	.0439	.00975	4.50	2510	(3.40)
1231 E	.0432	.01027	4.20	214	(2.33)
1231 F	.0427	.01068	4.00	111.8	(2.05)
1231 G	.0426	.01191	3.67	59.1	(1.77)
1231 H	.0459	.01482	3.10	28.6	(1.46)
1231 I	.0485	.01955	2.48	15.56	(1.19)
1231 J	.0492	.02200	2.24	12.34	(1.09)
1231 K	.0483	.02273	2.12	12.05	(1.08)
1231 L	.0473	.02355	2.02	10.49	(1.02)
1231 M	.0571	.0432	1.32	3.985	(0.60)
1231 N	.0633	.0555	1.14	3.62	(0.56)
1231 O	.0443	.00936	4.85	3125.	(3.50)

* To each mixture was added water to bring to a total net weight of 110 gm. of mixture.

** Measured by dip-in conductivity cell.

TABLE V. SUMMARY

RANGE OF COMPOSITION OF EQUILIBRIUM MIXTURES

LIQUID PHASE			SOLID PHASES			
% ZnO	% CrO_3	% H_2O	% ZnO	% CrO_3	% H_2O	Empirical Formula
0.0010	0.0012	99.998	-	0 to	?	ZnO·? H_2O and
			-	-	?	4.5 ZnO·CrO_3·?H_2O
0.0010	0.0012 to [M]	99.998	-	- to	?	4.5 ZnO·CrO_3·?H_2O to[M]
2.8	6.3	90.9	-	-	?	3.1 ZnO·CrO_3·?H_2O
2.8	6.3	90.9	-	- to	?	3.1 ZnO·CrO_3·?H_2O and
			54.5	33.5	12.0	2 ZnO·CrO_3·$2H_2O$
2.8 to 11.8	6.3 to 28.7	90.9 to 59.5	54.5	33.5	12.0	2 ZnO·CrO_3·$2H_2O$
11.8	28.7	59.5	54.5	33.5	12.0	2 ZnO·CrO_3·$2H_2O$
to 15.9	to 39.2	to 44.9	37.4	to 46.0	16.6	to [MM] ZnO·CrO_3·$2H_2O$
15.9 to 20.4	39.2 to 51.0	44.9 to 28.6	37.4	46.0	16.6	ZnO·CrO_3·$2H_2O$
20.4	51.0	28.6	37.4	46.0 to	16.6	ZnO·CrO_3·$2H_2O$ and
			-	-	?	ZnO·$2CrO_3$·?H_2O
20.4	51.0	28.6	-	- to	?	ZnO·$2CrO_3$·?H_2O
to 18.7	to [MM] 52.7	to 28.5	18.7	68.9	12.4	to [MM] ZnO·$3CrO_3$·H_2O
18.7 to 12.5	52.7 to 60.5	28.5 to 27.5	18.7	68.9	12.4	ZnO·$3CrO_3$·$3H_2O$
12.5	60.5	27.5	18.7	68.9 to	12.4	ZnO·$3CrO_3$·$3H_2O$ and
to 9.1	to 60.2	to 30.7	0	100	0	CrO_3
9.1 to 0	60.2 to 62.9	30.7 to 32.1	0	100	0	CrO_3

[M] Region of "solid solution".

[MM] Region in which route of changing composition is not certain.

TABLE VI

MICROSCOPIC DESCRIPTION OF CRYSTALS

Designation	Mole Ratio ZnO:CrO3	Method of Preparation	Description
521 D	4.1	Supersaturated solution was warmed to 25°C.	Yellow needles. 0.003 to 0.01 mm long.
522 X	Between 4.1 & 4.5	Saturated solution from 521 D was heated to 180°F and allowed to settle at 170°F.	Yellow needles. 0.01 to 0.04 mm long.
506 Q	3.9	Supersaturated solution was allowed to sit at room temperature.	Yellow needles. $<$ 0.001 mm long.
506 X	3.3	"	Yellow needles. 0.05 to 0.15 mm long.
506 R	3.1	"	Yellow needles. 0.002 to 0.003 mm long.
506 D	2.0	"	Clusters of very small orange-yellow particles
330 M	2.0	CrO3 solution added to ZnO slurry.	"
507 F	1.0	"	Very thin parallelograms with a 45° acute angle. Average dimensions 0.1 to 0.2 X 0.005 to .07 m.m. Red - Brown
316 U	1.0	ZnO slurry was added to a saturated solution	Thin parallelograms with 45° acute angle. Large variety of sizes.

TABLE VII

GRÖGERS DATA ON SOLUBILITY OF BASIC ZINC CHROMATES

Z. Anorg. Chem. 70, 135-144, (1911)

(1) Exp.No.	(2) CrO_3 (g/l)	(3) log (2)	(4) ZnO/CrO_3(molar) solid phase	(5) Conc.Soln.	(6) Solid Phases
1	0.010	Ī.000	32.2	Constant	2
2	0.010	Ī.000	16.7	"	2
3	0.010	Ī.000	6.90	"	2
4	0.604	Ī.781	3.98	Variable	1
5	2.14	0.330	4.00	"	1
6	4.19	0.622	3.97	"	1
7	11.4	1.057	3.50	Constant	2
8	11.5	1.060	3.31	"	2
9	22.2	1.346	2.99	Variable	1
10	31.4	1.497	3.00	"	1
11	43.1	1.634	2.98	"	1
12	57.5	1.760	2.99	"	1
13	66.5	1.823	2.43	Constant	2
14	66.7	1.824	2.20	"	2
15	70.6	1.849	1.990	Variable	1
16	93.3	1.970	1.976	"	1
17	101.	2.004	1.970	"	1
18	151.	2.179	1.972	"	1
19	192.	2.284	1.720	Constant	2
20	192.	2.284	1.611	"	2
21	285.	2.455	1.464	Variable	1
22	392.	2.593	1.470	"	1
23	450.	2.653	1.447	"	1
24	461.	2.664	1.322	Constant	2
25	463.	2.666	1.118	"	2
26	475.	2.677	.951	Variable	1
27	574.	2.759	.960	"	1
28	660.	2.820	.952	"	1
29	769.	2.886	.945	"	1
30	879	2.944	.952	"	1
31	970	2.987	.945	"	1