

THE THERMAL STABILITY OF VARIOUS SLIGHTLY SOLUBLE INHIBITIVE SALTS AND THEIR PROPERTIES

by
Edward R. Allen, Rutgers, The State University

Introduction

In the approach to the study of locating the optimum products, combinations, or set of conditions, in any large field, confusing complications arise because of dependent variables arising, in many cases, between different reactants and also because of combinations and permutations of various products under study. An important paper in the field of thermal stability of protective coatings by Fitzgibbon, Miller and Glaser¹⁰ covering an array of combinations of pigments and vehicles, illustrates the problems that can arise in such undertakings. The work covered in the present report, concerned solely with pigments for use in protective coatings, but with more emphasis on the chemistry of the phenomena involved, was still confronted with these difficulties.

The first products to be studied in this large field were the chromates, this because of the extensive background that has been built up in connection with their use in conventional inhibitive coatings. The products studied were chromate carrying combinations with zinc, cadmium, and the alkaline earths. These will be reported in the order named.

Chromates of Zinc

It is first necessary to review briefly the well known but frequently disregarded chemistry of these products on which some confusion still occasionally appears.

First, there are two types of chromate bearing zinc species, the complexes, of which zinc yellow (potassium zinc chromate) is best known, and second, the basic chromates of zinc. Zinc yellow corresponds to the composition shown by the formulas: $4\text{ZnO} \cdot 4\text{CrO}_3 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$ or $\text{K}_2\text{CrO}_4 \cdot 3\text{ZnCrO}_4 \cdot \text{Zn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Designation of this product as zinc chromate is incorrect. Zinc chromate, analogous to zinc sulfate, is so soluble that it is not conveniently obtained as the solid phase. However, zinc chromate readily complexes with potassium chromate to form the above potassium zinc chromate, which is sufficiently low in solubility to serve as the pigment. The British terminology, potassium zinc chrome, has much to commend it.

Potassium cadmium chromate, analogous to potassium zinc chromate, has been prepared by Cole and LeBrocq⁷ and evaluated in conventional inhibitive coatings by Cole,⁶ but was not specifically recommended for practical usage.

Of the basic chromates of zinc, zinc tetroxychromate, $5\text{ZnO}\cdot\text{CrO}_3\cdot 4\text{H}_2\text{O}$ or $4\text{Zn}(\text{OH})_2\cdot\text{ZnCrO}_4$, is the best known. This product was originally¹³ designated as a chemical compound, but as a result of a phase rule study,¹⁷ is now more elegantly expressed as a solid solution of the above components, and, what is of more interest, it was clearly shown that a series of compositions can be prepared which will vary continuously in solubility from the very low value of the familiar product to compositions of greater solubility than that of potassium zinc chromate, i.e., too high for satisfactory use as a pigment. These intermediate products have not been reduced to practice.

It is to be noted that another quite distinctive product, zinc monoxochromate, $\text{ZnCrO}_4\cdot\text{Zn}(\text{OH})_2$, has been disclosed by the British workers, Cole and LeBrocq,⁷ of the Royal Aircraft Establishment, Farnborough, Britain, and is now manufactured and used in Britain.

Dalton⁹ had already called attention to the lack of promise in thermal stability of zinc yellow. He showed that it became considerably darker and greener at 204.4°C with accompanying slight weight loss which gradually increased with increasing temperature and reached 3.39% at 260°C . Cole and LeBrocq⁸, on the other hand, reported stability, as judged by low weight loss, up to 380°C , with some evidence that this property varies with method of preparation. A sample was, therefore, prepared according to the procedures used by these workers and included in our experimental work in order to resolve this discrepancy, and to obtain additional information on the nature of the changes accompanying thermal decomposition, this because of their possible bearing on reactions with vehicles during the decomposition.

In the thermal stability studies the weight loss data were supplemented in some cases with chromate analyses. A sample of potassium cadmium chrome, stated by Cole and LeBrocq⁸ to be stable to 550°C , was also included. More specifically, Sample 37a was a laboratory preparation according to the procedure of Cole and LeBrocq,⁸ AF 39a, a representative commercial American product, and AF 38, a laboratory product prepared according to the disclosure of Tarr and Darrin.¹⁶ The potassium cadmium chrome AF 27a, was prepared according to Cole and LeBrocq.⁷

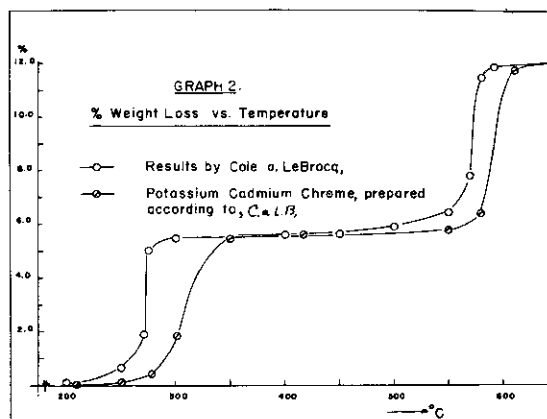
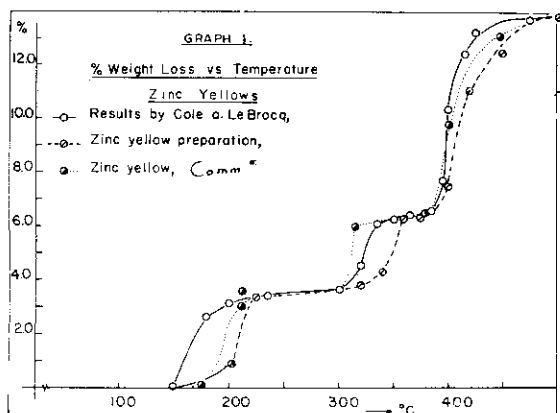
Contrails

Analyses showed the following compositions of these products:

	<u>%ZnO</u>	<u>%CrO₃</u>
AF 37a	38.21	45.21
AF 38	42.46	41.41
AF 39a	38.38	44.58
AF 27a		37.16

The percentage compositions of potassium zinc chromate calculated from the above formula is ZnO, 37.25; CrO₃ 45.78%, and the CrO₃ composition of the potassium cadmium chrome, 37.67%.

The results are included in Table I; those on zinc yellow are shown on Graph 1, and those on potassium cadmium chrome, together with results from Cole and LeBrocq⁸, on Graph 2.



The zinc complexes showed a perceptible greenish darkening at 250°C which gradually increased with increasing temperatures, with some sintering as 500°C was approached. The loss of chromium (VI) is comparatively small at 380°C but becomes very great at 500°, at which temperature sintering has begun.

The cadmium counterpart showed a behavior similar to that of zinc yellow but at slightly higher temperatures.

The results on zinc yellow are in general agreement with those reported by Dalton and fail to show any thermal stability properties of interest by this pigment.

TABLE I

Thermal Stabilities of Representative Potassium Zinc Chromates
and of a Potassium Cadmium Chromate

% Weight Loss⁺

AF-37a Cole-LeBrocq		AF-39a Commercial		AF-38 Tarr-Darrin		AF-27a K·Cd·Chrome Cole-LeBrocq	
°C		°C		°C		°C	
150	0.0	148	0.03	210	0.16	210	0.04
203	0.47	175	0.21	250	2.70	250	0.11
225	3.42	210	3.58	278	3.41	278	0.44
300	3.69	-	-	302	4.21	302	1.38
321	3.81	315	5.87	350	6.40	350	5.47
340	3.86	-	-	418	10.22	418	5.56
360	6.29	-	-	550	13.83	550	-
378	6.33	-	-	580	-	580	5.80
380	-	380	6.50 ^{oo}	612	-	612	11.86
400	7.69	400	-	-	-	-	-
420	10.83	-	-	-	-	-	-
450	12.12	447	-	-	-	-	-
476	13.55	-	-	-	-	-	-
502	13.96 ^o	-	-	-	-	-	-

+ Unless otherwise stated, the temperature data refer to one hour heating periods.

^o Sample showed 11.03% CrO₃ as compared with an original value of 45.21%.

^{oo} Sample showed 43.78% CrO₃ as compared with an original value of 44.58%

Contrails

Our methods of determining thermal stabilities were not quite the same as those used by Cole and LeBrocq,⁸ and while their findings were not confirmed as to higher thermal stability of certain products, the inference that their results are erroneous is not in order. However, the conclusion is justified that any improvements in thermal stability of potassium zinc chromate resulting from variations on preparative methods are of minor significance and, therefore, not of interest in this program. Likewise, the potassium cadmium chromate, while showing some superiority over the counterpart zinc complex, the difference was not sufficient to justify further study of the cadmium complex.

No observations were made on the possible catalytic reactions with vehicles as a result of thermal decompositions, although it is possible that the green colorations beginning around 250°C, caused presumably by the reduction of chromium (VI), might give rise to such secondary reactions in certain cases.

The basic chromates of zinc were represented in this study by a commercial zinc monoxchromate, AF 40c, obtained from a British manufacturer (59.35% ZnO, 35.00% CrO₃), and by an American commercial zinc tetroxchromate, AF 41c, (71.17% ZnO, 79.31% CrO₃). The data on behavior of these on heating is shown in Table II, and depicted in Graph 3.

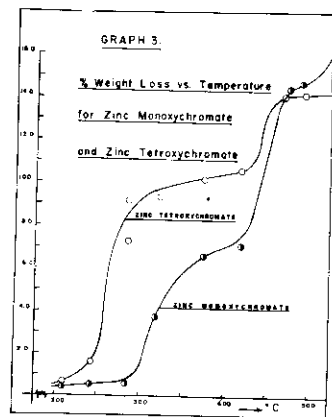


TABLE II

Thermal Stabilities of Basic Chromates of Zinc

<u>Temperature</u>	<u>Sample AF-40c⁺</u>	<u>Sample AF-41c⁺⁺</u>
°C	Monoxychromate	Tetroxochromate
210	-	-
242	0.54	1.43
285	0.56	9.16
320	-	-
375	6.64	10.28
419	-	-
468	14.43 ^o	14.16
492	14.60	14.23 ^{oo}
530	-	-

+ Sample turned olive green at 285°C to 320°C and became dark and purplish in the 375°C to 530°C range.

++ Sample showed some greening at 242°C and purplish gray at 375°C.

o Sample c showed 1.47% CrO₃ compared with the original value of 35.00%.

oo Sample c showed 1.34% CrO₃ as compared with 17.39% originally.

Thus, there is no meritorious thermal stability shown by these products; the weight losses were marked as 500°C is approached, at which temperature range color change and the loss in chromium (VI) becomes very substantial. These products, therefore, were not studied further. It is to be noted, however, that the presence of basic material in these compositions does not alter the degree and type of the decomposition, a factor of major importance in the alkaline earth chromates as pointed out below.

ALKALINE EARTH CHROMATES

a. Calcium Chromate

The first point to visualize in considering this compound as a pigment is that it varies widely in solubility, depending largely, although apparently not entirely, on the amount of water of crystallization in the molecule. The method of preparation is, it is now realized, quite effective in dealing with this property of solubility. An unknown amount of the past evaluation work on calcium chromate has been based on the high solubility type illustrated, e.g., by Pigment No. 12, listed below in Table III and probably responsible for statements, such as that of Bearn⁴, ascribing to it a very low rating as a pigment. It is to be noted that Fitzgibbon, Miller and Glaser¹⁰ rated calcium chromate as the best of the considerable range of pigments they studied. A sample from the same source which they report showed in our work an equilibrium solubility of 1.03% as compared with 1.06% for our laboratory preparation, AF-29, used in obtaining the data reported in Table IV. It is our belief, therefore, that the product they used was of the low solubility type. It is our further thought that they would not have given calcium chromate the high rating they did were the material of the high solubility type.

The work of LeBrocq and Cole¹², giving specific procedures for preparing the anhydrous material of low solubility, has been a most important contribution to this confused picture, especially as applies to the pigment field, although much remains to be done to completely clarify the overall picture of the hydrates of calcium chromate. For reasons stated below the type product represented by Pigment No. 11, shown in Table III, is regarded as best suited for pigment work.

The data on range of solubilities possible, taken from the work of Cole⁶, are shown in Table III.

TABLE III

Equilibrium Solubilities of Calcium Chromates

<u>Pigment No.</u>	<u>Pigment</u>	<u>Source</u>	<u>Solubility</u> ^o
10	Calcium Chromate	R.A.E.‡	0.46
11	Calcium Chromate	R.A.E.	1.40
12	Calcium Chromate	R.A.E.	6.6
13	Strontium Chromate	Laboratory re-agent	0.06

‡ Royal Aircraft Establishment

^o Unless otherwise stated all results on solubility in this paper are expressed as g CrO₃/100 ml. of supernatant liquid.

TABLE IV

Thermal Stability of Calcium Chromate

Weight Loss Data for AF-29

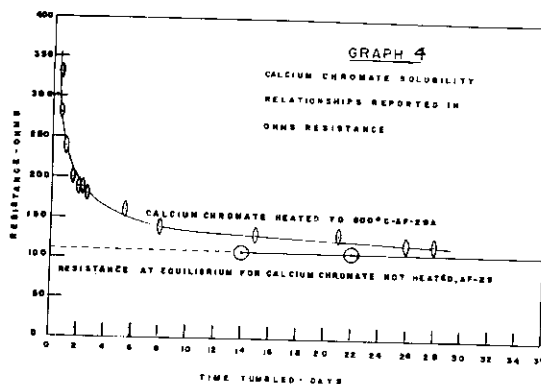
<u>Temperature</u>	<u>Weight Loss</u>	<u>Color</u>
°C	%	
300	-	Yellow
400	.62	Yellow
600	1.47	Yellow
750	1.83	Yellow-green
800	1.88	Pale green
950	2.04	Pale green
1000	7.06	Fused and blackened

Contrails

The reference material AF-29, 96% purity, used in thermal stability determinations, was a laboratory preparation according to the disclosure of LeBrocq and Cole¹², and is the same type as Pigment No. 11 in the preceding table. It was anhydrous and showed an equilibrium solubility of 1.06%. Its behavior on heating is shown in Table IV.

The first evidence of alteration with rising temperature is shown by the slight greenish coloration at 750°C. This and the weight loss increase slightly up through 950°C. In this particular experiment the decomposition was viewed as essentially complete at 1000°C, as evidenced by the marked weight loss, fusing and blackening of the specimen, a hard sintered mass devoid of pigment properties. This result was rather surprising since it is reported in the Bangalore work that pure calcium chromate is stable at 1000°C. However, repeats confirmed the lack of stability in the 1000°C-1100°C range. Calcium chromate does show, however, a marked superiority in thermal stability over any of the chromate carrying species of zinc or cadmium.

The statement of LeBrocq and Cole¹² was confirmed that on baking the anhydrous material at 400-600°C a product of lower solubility results. A subsample of AF-29, designated as AF-29a was heated for one hour at 600°C and the resulting product showed a distinctly lower solubility as shown by the higher ohmic resistance of the aqueous solution suspension. This solubility increased with time on tumbling in a thermostat, reaching essentially that of the unheated sample, AF-29, in 28 days. The results are shown on Graph 4. The reduced solubility obtained by baking is probably a case of metastability. The use of this product in coating compositions is viewed with skepticism.



b. Strontium Chromate

Fitzgibbon, Miller and Glaser¹⁰ gave strontium chromate a high rating, although not quite the equal of that given to calcium chromate. In earlier work in this laboratory² calcium chromate appeared to be the more promising of the two, although it was recognized that, because of the marked influence of impurities present, this rating might be changed by systematic study of preparative methods.

In the present program, just as in the case of calcium chromate, strontium chromate showed some distinctive chemical behaviors, although of a quite different nature. Failure to understand these properties, it is submitted, has contributed to retarding the more general use of this product. Simple as it may seem, and this is revealed in the purely chemical and in the applied literature, considerable difficulty arises in preparing this product. This is apparently due, in part at least, to the tendency of the strontium to form complexes, and, therefore, to disturb the stoichiometric balance. Consequently, it proved necessary to determine purity of samples by analyses for both strontium and chromate. The former required the development of a special method. This was based on the principle that (a) chromate ion in dilute solution is not adsorbed by Dowex 50, and (b) the alkaline earth cations after elutions may be titrated with ethylene diamine tetra-acetic acid (EDTA)⁹. The following five samples, four laboratory preparations and one commercial product, show something of the variations encountered in this product.

AF-13 - from strontium chloride and potassium chromate. Spectroscopic examination failed to show the presence of potassium, i.e., complexes with this element were non-existent.

AF-15 - from sodium chromate and strontium chloride by carefully controlled precipitation, charge adjustment and washing, to prevent formation of basic materials, i.e. complexes.

AF-16 - precipitation by the simultaneous addition of chromic acid and strontium hydroxide to the boiling charge with flow adjustment to the neutral point.

AF-17 - a commercial sample, American market.

⁹ Devised by Dr. Julius Ciric

Contrails

AF-33 - similar to AF-15, but with the preparative procedure modified to permit the formation of a small amount of basic material.

The compositions of these samples are recorded in Table V. The higher values of purity obtained by EDTA analyses over those by chromate analyses are designated, for want of a better term, as "Strontium Overages"

Sample AF-16 is recognized as an abnormal composition probably resulting from errors in the preparative technique, nevertheless, it does contain a large excess of strontium, probably basic complexes, and in Table VI, illustrates the effect of the presence of basic materials.

As was shown in the Bangalore work³, the presence of oxides of alkaline earths contributed definitely to lowering the decomposition points of the corresponding chromates as judged by the development of green coloration. By way of appraising such reactions, the three samples in Table VI were heated for one hour periods at increasing temperatures up to and including 1000°C with the percent weight losses shown in Table VI. The values for "strontium overages" are reported to illustrate the influence of basic materials.

TABLE V

Compositions of Representative Strontium Chromate Samples

<u>Sample AF-No.</u>	<u>% SrCrO₄ determined Chromate Analyses</u>	<u>By EDTA Titration</u>	<u>Strontium "Overage"</u>
13	98.92	99.26	
15	99.02	98.85	0.34
16	90.64	102.05	-0.17
17	95.33	97.38	11.41
33	98.29	100.12	2.03
			1.83

TABLE VI

Weight Losses of Different Samples of Strontium Chromate

No.	Sr. Overages	100°C	300°C	400°C	600°C	750°C	800°C	1000°C [‡]
AF-15	-00.17	0.08	0.36	0.40	0.55	0.59	0.59	0.61 ⁺
AF-16	11.41	0.07	0.47	0.66	0.74	3.85 ⁺	3.34 ⁺	3.61 ⁺
AF-17	2.03	0.048	1.37	1.71	2.01 ⁺	2.12 ⁺	2.12 ⁺	1.86 ⁺

‡ - Four hours of heating.

+ - Samples became light green in color.

A petty but annoying source of error in dealing with strontium chromate, until it was pinned down, was the difficulty in obtaining a constant weight on oven heating in analytical work. Strontium chromate samples will usually show creeping weight losses at 110°C for over 200 hours. Disregarding this has apparently been acceptable in ordinary applied work, but was not permissible in this more exacting program. After several series of tedious determinations it was established that (a) the creeping losses up to 400°C were due to the elimination of water as shown by the Penfield method¹⁵ and (b) laboratory preparations reach a constant weight in one hour, at 300°C.

Sample AF-33, used in this particular experiment, showed a percent weight loss at 1 hour at 110°C of 0.2214%; this gradually increased up to 235 hours when constant weight was realized and a weight loss of 0.362%. Continued heating at 300°C for 19 hours showed no further loss. Other laboratory samples behaved similarly.

AF-17, the commercial sample, behaved slightly differently in that it did not reach constant weight at 300°C in 1 hour, but did do so in 4 hours. One hour at 400°C gave a slightly greater weight loss, which did not change on continued heating at this temperature. These latter differences, i.e. between 300°C and 400°C, are very slight indeed and can be ignored except in the most exacting work. Our tentative analytical procedure, therefore, is drying one hour at 300°C.

Determinations of the thermal stability of strontium chromate were made on sample AF-13. Five sub-samples,

Contrails

AF-13-0 to AF-13-4, were used for the determinations shown in Table VII.

TABLE VII

Behavior of Strontium Chromate AF-13 Samples on Heating

<u>Sub-Sample No.</u>	<u>Time Hr.</u>	<u>Temp. °C</u>	<u>Wt. Loss Total %</u>	<u>SrCrO₄*</u>
AF-13-0	1	750	0.80	98.39
	1	800	0.81	
	4	1000	0.82	
AF-13-1	1	110	0.03	97.84
	1	300	0.31	
	1	400	0.59	
	1	600	0.69	
	4	1000	0.82	
	8	1000	0.82	
	12	1000	0.82	
AF-13-2	1	110	0.05	98.18
	1	300	0.28	
	1	400	0.60	
	1	600	0.67	
	4	1000	0.83	
	8	1000	0.84	
AF-13-3	1	300	0.41	98.92

* Calculated from iodometric determination of chromium (VI) on the heated samples.

These results show an unmistakable superiority of strontium chromate over calcium chromate. All samples showed a slight greenish coloration at the 1000°C heating, presumably due to the formation of some chromium (III) from chromium (VI). The amount, however, so transformed, as shown by the analytical data, is very small. It is relevant to note the checks on drying at 300°C for 1 hour and also the fact that the weights remain constant at 1000°C for periods of up to 8 hours. Behaviors of temperatures above 1000°C are reported later.

AF-15 carries no excess of strontium, i.e., no basic material, and first shows a slight greening at 1000°C. Large and moderate excesses are shown by AF-16 and AF-17, respectively, and that these contaminants influence the weight losses and greenish colorations

markedly is clearly shown. That AF-17 with a lower strontium excess shows a color change at a lower temperature than does AF-16 is believed to be due to the presence of a small amount of a soap-like substance presumably added by the manufacturer to obtain the good texture which characterized the product. That this may be a calcium soap is indicated by the spectroscopic examination which showed unmistakable presence of calcium, but which, however, proved to be scarcely measurable by quantitative analytical procedures.

ALKALINE EARTH CHROMITO-CHROMATES

Patterson and Sloan¹⁴, possibly from suggestions arising from the Bangalore work³, disclosed the alkaline earth chromito-chromate type of pigment, obtained by roasting at 900-1100°C an intimate mixture of controlled amounts of an alkaline earth chromate and an alkaline earth oxide or compound which is heat-decomposable to the oxide.

It is in order to note here that the exact chemical and physical nature of chromito-chromates is not known. The term is unfortunate since the term chromito suggests chromites, whereas chromites apparently do not enter into the composition as such, since only insignificant percentages of acid insoluble material are formed in the 1000°C-1200°C range. Evidence based on color change, chemical analysis, and X-ray analysis, supports the idea that a change, from yellow to green, indicates the transformation of some chromium (VI) to chromium (III). Presumably the chromium (III) is ionically bound in some way to the chromate.

But whatever the nature of the reaction, the results reported above on the influence of basic impurities on the behavior of calcium and strontium chromates on roasting is viewed as a case of the formation of these chromito-chromates. Designating this as decomposition is somewhat misleading.

Orientation results on roasting at 950°C had shown the following effects of this operation on equilibrium solubilities:

<u>Sample</u>	<u>Solubility</u>
CaCrO ₄	1.0602
CaCrO ₄ :CaO, 3:30:1	0.8971

Contrails

These values are viewed as scarcely beyond the experimental error that existed. These findings are at variance with those of Patterson and Sloan. As suggested above, however, the original calcium chromate used by these workers was different than that used in this program. Moreover, their values on solubility were obtained on leachings from coatings containing the pigments under evaluation. Interesting as these values are, they are not equilibrium solubilities. Because, however, of the distinctly higher thermal stabilities shown by strontium chromito-chromate as compared with the calcium counterpart, further studies on the solubilities of the latter were not made.

Strontium chromate and chromito-chromate showed the following behaviors under roasting in the 900°C-1100°C range:

<u>Sample</u>	<u>Solubility</u>
SrCrO ₄	0.0519
SrCrO ₄ :SrO:2.58:1	0.0855
SrCrO ₄ :SrO:2.66:1	0.1107

Patterson and Sloan claim for these new products, particularly for the calcium compositions, which they studied the most extensively, much lower solubilities in the case of calcium chromito-chromate as compared with calcium chromate.^o

^o The work of LeBrocq and Cole^{1,2}, disclosing a satisfactory process for obtaining the low solubility type of calcium chromate, was not then available, hence the comparison was with the high solubility type.

They also showed that on roasting in the 900°C-1100°C range, solubilities decreased with the increasing CaO/CaCrO₄ ratio, and that this progressive change was associated with increased greenness in shade of the pigment. It seemed, therefore, a reasonable expectation that products prepared in the above range would be stable at those temperatures. This, together with other properties claimed, justified including the study of these products in the temperature ranges above 1000°C.

A number of new obstacles arose in connection with this phase of the program. These were mechanical and chemical. One of the former was the choice of suitable furnacing equipment. The electric muffle type of furnace

Contrails

heretofore used had proven reasonably satisfactory but when the attempt was made to explore temperatures above 1100°C, difficulties began to be encountered. Temperature distribution in the muffle lacked uniformity and this became more apparent as the temperatures were increased. More serious than this, the equipment of this type would not stand continued usage at temperatures above the 1200°C-1300°C range. Considerable information was obtained with this equipment which proved inconsistent, and on cross checking, was in some cases definitely unreliable, therefore, is not formally reported. However, the data reported below and obtained with the muffle furnace are believed to be reliable.

A second mechanical difficulty arose in connection with the ball milling of strontium chromate-strontium oxide (or hydroxide) compositions. Dry milling was necessary to properly cover an appreciable range in compositions. The first experiment showed a surprising segregation of components; the ratios determined by analysis were quite different from those compounded originally. Nevertheless, the following results are of some interest in that they again showed a slight increase in solubility on roasting at 1000°C.

Muffle Furnace

<u>Ratios</u> SrCrO ₄ : SrO	<u>Solubility</u>
1 : 0	0.046
1.5 : 1	0.069
10 : 1	0.069
16 : 1	0.051

Here again the differences are scarcely beyond experimental error, and not of significance to this program.

The difficulty in ball milling was finally overcome by pre-roasting of the strontium chromate, and also very thorough mortar grinding of very small samples gave satisfactory compositions. The chemical difficulties in exploring the chromite-chromates arose from the veritable avalanche of possible reactions suggesting study. The influence of varying ratios of components, the possibilities of the formation of mixed crystals, or solid solutions, the possible permutations and combinations of the large number of compounds and complexes presented a bewildering array of experimental possibilities. By focusing efforts on those properties and behaviors relevant

to the objectives of this program results of interest were obtained. The explanations of the reactions involved were scarcely touched.

The chemical changes as judged by chromate analyses of the resultant roasted compositions were then carried out with the results shown in Table VIII.

TABLE VIII

Behaviors of Chromito-Chromate on Roasting

All ratios of chromate to oxide, 10:1

<u>Sample</u>	<u>Temp. (°C)</u>	<u>Cr(III)/Cr(VI)*</u>
SrCrO ₄ :SrO	1000°C ⁺⁺	.054
SrCrO ₄ :SrO	1100°C ⁺⁺	.042
SrCrO ₄ :SrO	1000°C	.059
SrCrO ₄ :SrO	1100°C	.052
SrCrO ₄ :CaO	1000°C	.033
SrCrO ₄ :CaO	1100°C	.065

* These values were obtained by determining the Cr(VI), oxidizing Cr(III) to Cr(VI) to obtain total Cr, Cr(III), therefore, by difference; e.g. the first sample showed Total Cr, 254.48 mgs, Cr(VI) 241.4 mg, Cr(III) 13.08 mg, whence $\frac{13.08}{241.4} = 0.054$

++ Mortar Ground

Although the data indicate that the chromito-chromates change to a greater degree than does pure strontium chromate, the alteration in either case was very slight. It is worth noting that the laboratory preparation of strontium chromate, AF-47, showed 98.6% purity by chromate analysis and 98.53% by strontium analysis, stoichiometrically balanced therefore. This sample on roasting at 1000°C showed only a very slight greenish coloration. Analysis for Cr(III) gave a zero value, i.e., was not analytically detectible. Thus the Cr(III) obtained in the above experiments was all due to the action of the basic material present in the compositions.

Up to this point, in the face of the difficulties reported above, roasting had been carried out in the electric muffle furnace. As the work was extended to higher temperature ranges, activities were centered on

Contrails

the induction furnace.^o This equipment was placed in good working order with the help of the manufacturer. It proved necessary to use the quite expensive zirconium silicate type of crucible. Only small samples, approximately 5 grams, were used. Temperatures were measured by an optical pyrometer. Duplicate, and, in some cases, triplicate tests were made. The results were reasonably consistent and, therefore, believed to be reliable.

The behaviors of calcium chromate and calcium chromito-chromate on roasting were checked with the new induction furnace technique with the finding that both products show a fusion breakdown in the 1000°C-1100°C range with no essential difference between them. While there were indications from the work of Patterson and Sloan, and from that at Bangalore as well as from our own exploratory work, that such behaviors would vary with the $\text{CaCrO}_4:\text{CaO}$ ratio, the evidence was that this effect would be relatively minor; clearly not enough to equal the thermal stability of the strontium counterpart, consequently, further study of this set of variables was not pursued.

A sample of commercial barium chromate, and of the relatively new commercial product, Basic Lead Silico-chromate, was included in this study.

The results reported in Table IX, showing the fusion ranges of the high temperature candidates, and the important changes accompanying this fusion, have been obtained as a result of a large amount of work and are believed to be reliable.

The alkaline earth chromates tested show relatively high thermal stabilities; that of SrCrO_4 was a pleasant surprise. It is interesting that even after fusion they all contain appreciable amounts of chromium (VI).

It is also to be noted that the Cr(III) produced is higher than that obtained at the 1000°C-1100°C range, and that the amount of Cr(III) formed in the chromito-chromate composition is definitely higher than is the case with the strontium chromate, although the temperature is 105°C lower.

The absence of data for $\text{SrCrO}_4/\text{CaO}$ (10:1) and for barium chromate is attributed to interference in the analysis of chromium (III) and strontium by material from the zirconium silicate crucible. However, no interference was encountered in the analysis of chromium (VI).

^o Ajax-Northrup Frequency Converter, Electrothermic Corp., Trenton, New Jersey.

TABLE IX

Behaviors of Chromates at the Fusion Range

<u>Compound or Mixture</u>	<u>Fusion Range</u>
Basic lead silico-chromate, M-50	1475 - 1490°C
SrCrO ₄ , AF-47	1380 - 1390°C
BaCrO ₄	1345 - 1355°C
SrCrO ₄ :SrO (10:1)	1280 - 1285°C
SrCrO ₄ :CaO (10:1)	1265 - 1270°C

Changes in Chromium Compositions

<u>Fused Materials</u>	<u>Cr(III)/Cr(VI)</u>	<u>Cr(VI)/alk Earth</u>
SrCrO ₄ , AF-47; 1390°C	.106	.647
SrCrO ₄ :SrO (10:1); 1285°C	.410	.520
SrCrO ₄ :CaO (10:1); 1350°C	-	-
BaCrO ₄	-	.708

Detailed X-ray examinations made of the strontium chromate samples, AF-33 and AF-47, before and after heating at 1000°C, 1100°C and at fusion temperatures showed scarcely detectable changes even on fusion, although, at this last point, a very slight greenish coloration appeared.

Corresponding examinations of the strontium chromite-chromate SrCrO₄:SrO, 10:1, showed the formation of a new product, analagous to the behavior of the calcium counterpart, but with the distinct difference that the strontium chromate pattern does not disappear. Whether strontium oxide also disappeared could not be determined because of lack of distinctive lines in the powder diagram. The experiment was repeated with different preparations and increasing temperatures, with the same result. Even in the fused sample strontium chromate and a new product are still present, although there are indications the new product is not the same in the fused as in the samples roasted in 1000°C and 1100°C.

Barium chromate showed no change, detectable by x-ray examination, on the fused sample. In contrast, basic lead silico-chromate showed complete loss of original pattern on fusion, but showed the highest fusion point of any product examined.

Solubility

The determination of solubilities of various products has proven helpful throughout this program. Conductivity measurements have been of assistance primarily as an indication of equilibrium between the solid and the aqueous phases. The data on solubilities are expressed as chromate equilibrium solubilities.

Several instances have been noted in which solubility data have been delayed because of gradual changes in conductivity readings indicating that these systems were not completely in equilibrium. Moreover, observations on a number of these samples indicate that the changes in the conductivity measurements are not related solely to the degree of solubilization of the chromates but may be caused by other phenomena. A detailed study of the solubilities of these materials would be very time consuming and did not appear to be warranted, especially since all the solubilities fall within the range that is regarded as acceptable in inhibitive pigment usage.

The data reported in Table X are representative of results that obtained near the termination of the study of the chromates.

TABLE X

Effect of Roastings on Representative Chromates

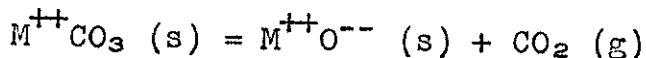
<u>Sample</u>	<u>Roasted at</u>	<u>Solubility</u>
SrCrO ₄ , AF-47	1000°C	.041
SrCrO ₄ :SrO (10:1)	1000°C	.040
SrCrO ₄ :SrO (10:1)	1100°C	.041
SrCrO ₄ :SrO, (10:1)	1000°C	.043
SrCrO ₄ :CaO (10:1)	1000°C	.067
SrCrO ₄ :CaO (10:1)	1100°C	.069

The above data are in accord with the generally recognized low water solubility of strontium chromate. That no increase in solubility of the chromite-chromate over the chromate, whereas previous results had shown a slight increase, is attributed to experimental error. However, an unmistakable increase in solubility is shown by the strontium chromate-calcium oxide roasted compositions.

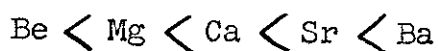
Factors in the Stability of Alkaline Earth Salts Carrying Polyatomic Anions

The stability of alkaline earth salts with polyatomic anions, such as the carbonate, is a function of the ionic radius of the cation.

Thus for the reaction:



The stability as measured by the temperature at which equal pressures of carbon dioxide are produced is in the order:



A consideration of a cycle of the Born-Haber^{5,11} type^o

^o See also Moeller, Inorganic Chemistry, 184, Wiley, 1952

shows that the stability is governed by several factors of which the ionic radius of the cation is of great importance, since it determines the lattice energy U_0 . If ionic size is plotted against U_0 , for the oxide and for the carbonate, it is found that the oxide is favored with respect to stability more for beryllium than for barium, and that stability is in the order indicated above.

The trends observed in this investigation are viewed as in harmony with the Born-Haber cycle. While it was found that strontium chromate showed a slightly higher fusion point than did barium chromate, it is to be noted that the latter compound did not undergo detectable chemical decomposition at this fusion point. Because of the tentative decision that barium chromate was unsuited for the Air Force requirements because of lack of other pigment properties, the exact decomposition point of barium chromate was not determined.

Discussion and Summary

The sifting of the evidence on the thermal stabilities of the chrome carrying pigments, those of zinc, of cadmium, and of the various alkaline earths, leads to the conclusion that strontium chromate is the preferred product.

One quite clear cut difference between the zinc and cadmium products on the one hand and those of the alkaline earths on the other, **whereas in the former, the reduction of chromium (VI) becomes progressive with rising temperatures, whereas in the case of the latter this type of change proceeds to a certain degree and stops abruptly until final fusion takes place.**

In the case of the calcium derivatives, x-ray determinations showed clearly that, in roastings of $\text{CaCrO}_4:\text{CaO}$ composition, the patterns of both components are replaced by that of a new product. The differences in solubilities between the calcium chromate and calcium chromito-chromate are rather small. Both the calcium chromate and chromito-chromate fuse in the 1000°C - 1100°C range, i.e., far below the fusion point for the strontium counterparts. Conceivably, evaluations by applied workers may show properties of merit by the calcium products. If so, the information is now available to enable manufacturers to produce such products. The solubilities of calcium chromate can now be readily controlled, and the calcium chromito-chromate can be readily manufactured provided volume business is in sight.

The strontium chromito-chromates, the basis of a more extended investigation, have also been rejected. These products are slightly lower in thermal stability and possibly very slightly higher in solubility than is the case with strontium chromate. X-ray analysis showed that in the roasting of $\text{SrCrO}_4:\text{SrO}$ compositions a new product is formed, but that even on prolonged calcinations, the strontium chromate did not disappear. This means dealing with an incomplete reaction and a mixture of unknown substances from a reaction which is itself very incompletely understood. Hence, the rejection of this product or group of products.

Essentially pure strontium chromate has a fusion range of 1380°C to 1390°C while that of the chromito-chromates is approximately 100°C lower. The roasted, and even the fused materials, contain sufficient soluble Cr(VI) to show distinct corrosion inhibitive properties.

Contrails

Barium chromate has a fusion range of 35°C to 40°C lower than that of the strontium chromate. X-ray determinations showed, interestingly enough, that appreciable decomposition did not accompany this fusion.

Basic lead silico-chromate M-50 has a fusion range of about 100°C higher than that of strontium chromate, and is, consequently, the pigment with the highest fusion point observed in this study. However, the x-ray determinations show that practically complete decomposition accompanies this fusion. The viewpoint was that neither the barium chromate, nor the basic lead silico-chromate will be suitable as inhibitive materials for the Air Force because of their very low solubility.

Thus strontium chromate, originally viewed with skepticism,² now emerges as the superior product of this study. However, the following shortcomings may have contributed to its lack of more general usage.

In the first place, unless special care is taken in the preparation of strontium chromate, the product will contain varying amounts of basic materials, as shown by the lack of stoichiometric balance, hence the "strontium overages" observed. The presence of these basic materials, or of strontium oxide, hydroxide or carbonate, even in very small amounts, has a marked effect in lowering the thermal stability of the product, as judged by the development of greenish colorations. In all such cases examined this color change was shown to be due to the formation of some Cr(III).

This puzzling behavior was observed in the early work² wherein it was observed that the percentage of Cr(III) formed on heating to 750°C varied inversely as the purity. This is now more clearly understood and is viewed as a case of the formation of a small amount of strontium chromito-chromate, not true decomposition.

It is emphasized that, so far as observations of this program are concerned, there is no certainty that this greenish coloration, characteristic of the alkaline earth chromates, is objectionable other than the consumption of Cr(VI). On the other hand, it likewise is not known that it would be without influence on certain coating compositions at elevated temperatures.

Another undesirable property of strontium chromate is the slowness with which it reaches constant weight in the drying operation. This can be dealt with

Contrails

analytically by the recommended procedures.

Strontium chromate tends to be harsh in texture. No systematic study was made of this property in this program. The one commercial sample examined, AF-17, of acceptable texture, was believed to contain a dispersing agent, possibly of the soap type.

These shortcomings are of the type, however, that can be overcome by proper study and can be readily mastered by pigment manufacturers. In other words, no serious procurement problem appears to exist. The net conclusion, therefore, is that strontium chromate merits careful consideration as an inhibitive material of high thermal stability.

BIBLIOGRAPHY

1. Allen, E. R. and Ciric, Julius, "Investigation of the Thermal Stability of Various Slightly Soluble Salts and their Products", WADC Technical Report 59-14, January 1960, p. 32.
2. Allen, E. R. and Lindstrom, H. V., "The Investigation of Thermostability of Inhibitive Pigments", WADC Technical Report 57-752, March 1958.
3. Bangalore, India, Investigations: A series of 20 papers by Nayar, Nargund, Athavale, Datar, and their associates, published in the Jour. of the Indian Inst. Sci., Section A 7-23A, (1924-1941). This program concerned with the reactions involved in, or relevant to the calcination of crude chromite ores, contains much material on the chromates of the alkaline earth.
4. Bearn, "Chemistry of Paints, Pigments and Varnishes", p. 159, 1923.
5. Born, Ber. deut. phys. Ges. 21, 679 (1919).
6. Cole, H. G.: "Tests on the Relative Efficiency of Chromate Pigments in Anti-Corrosive Primers", Royal Aircraft Establishment, Farnborough, Technical Note Met. 185 (November 1953); J. Appl. Chem., 5, 197 1955.
7. Cole, H. G., and LeBrocq, L. F.: "The Chemistry of Some Complex Zinc and Cadmium Chrome Pigments", Royal Aircraft Establishment, Farnborough, Technical Report Met. 75, (September 1953); J. Appl. Chem., 5, 149 (1955).
8. Cole, H. G., and LeBrocq, L. F.: "The Thermal Decomposition of Complex Zinc and Cadmium Chromes", Royal Aircraft Establishment, Farnborough, Technical Note Met. 242 (May 1956).
9. Dalton, A. S.: "The Use of Basic Magnesium Chromate Pigment in Corrosion Inhibiting Primers", WADC Technical Report 58-199 (1959).

Contrails

10. Fitzgibbon, C. R., Miller, E. H., and Glazer, M. A.: "High Temperature Protective Coatings for Magnesium", WADC Technical Report 56-222, page 32 (1957).
11. Haber, F., Ber. deut. phys. Ges. 21, 750 (1919).
12. LeBrocq, L. F. and Cole, H. G.: "Improvements in the Manufacture of Calcium Chromate", B. P. 552, 685 (1943), U.S.P. 2,346,493 (1944).
13. Leisey, R. W., Zinc Chromate, U.S.P. 2,251,846 (1941) Kittleberger, W. W., Zinc Tetroxochromate, "A Rust Inhibitive Pigment.", Ind. Eng. Chem. 34, 363 (1942).
14. Patterson, G. D., and Sloan, C. K., "Basic Alkaline Earth Chromito-Chromate Pigment and Method of Making." U.S.P. 2,387,528 (1945).
15. Penfield, S. F., Am. Jour. Sci., 3rd. Ser. XLVII, p. 30 (1894).
Hillebrand, W. F., "The Analysis of Silicate and Carbonate Rocks", U. S. Dept. Interior, Bull. 700, p. 77 (1919).
16. Tarr, O. F. and Darrin, M.: "Process for Preparing Zinc Yellow Pigments", U.S.P. 2,415,394 (1947).
17. Woodward, A. E., Allen, E. R., and Anderson, R. H., "A Phase Rule Study of the System Zinc Oxide-Chromium Trioxide-Water at 25°C," Jour. Phys. Chem. 60, 939 (1956).