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THERMAL DECOMPOSITION OF ZINC CHROMATES*

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ABSTRACT

A study of the thermal decomposition in air of zinc chromates from several sources was conducted using thermogravimetry, chemical analysis, emission spectroscopy and X-ray diffraction analysis. Four zinc chromate samples were obtained from commercial suppliers and four others were prepared in this laboratory. The zinc chromates were identified as various materials depending on the method of preparation. Compounds either identified or postulated included $4ZnCrO_4 \cdot K_2O \cdot 3H_2O$ (I), $2ZnO \cdot CrO_3 \cdot H_2O$ (II), $4ZnO \cdot CrO_3 \cdot 3H_2O$ (III), $ZnCrO_4$ (IV), $5ZnO \cdot 5CrO_3 \cdot Na_2O \cdot 3H_2O$ (V) and $5ZnO \cdot 4CrO_3 \cdot Na_2O \cdot 5H_2O$ (VI). Upon heating to 900°C, compound I underwent a four step decomposition to form ZnO, $ZnCr_2O_4$ and K_2CrO_4. Compounds II and III each decomposed in two steps to form ZnO and $ZnCr_2O_4$. The thermogram for compound IV showed only a single step with the final products also being ZnO and $ZnCr_2O_4$. The decomposition of compounds V and VI each involved two steps with the formation of ZnO, $ZnCr_2O_4$ and Na_2CrO_4. Chemical analyses gave assay values for the zinc chromates ranging from 40.2 to 96.9% $ZnCrO_4$.

INTRODUCTION

Because of the use of zinc chromates as depolarizers, or active cathode materials, in thermally activated voltaic cells operating at temperatures in excess of 450°C, the properties of zinc chromates are of value. In order to efficiently design such thermal cells, to effectively and reproducibly prepare the depolarizer material, and to accurately analyze cell discharge data, it is important to have a knowledge of the composition and the thermal stability of the zinc chromates. Thermogravimetry, X-ray diffraction analysis, chemical analysis and emission spectroscopy have been used to obtain the desired information. The goals of this program were: (1) to determine the composition of a variety of zinc chromate samples and (2) to study the thermal decomposition of these samples.

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EXPERIMENTAL

Materials

Zinc chromate was obtained from four different suppliers and also prepared in our laboratories by four different methods. The suppliers and labeled purity of the commercial samples are shown in Table 1.

TABLE 1
COMMERCIAL ZINC CHROMATES INVESTIGATED

Supplier	*Labeled purity*
City Chemical Corporation	zinc chromate, purified powder
Fisher Scientific Company	zinc chromate, purified powder
Frank D. Davis Company	zinc chromate
Research Organic/Inorganic Chemical Corporation (Roc/Ric)	zinc chromate, $ZnCrO_4 \cdot 7H_2O$, 99%

Four zinc chromate samples were prepared in our laboratory by the following procedures.

Sandia-1: solutions of 2.0 M $ZnCl_2$ and K_2CrO_4 were prepared from reagent grade chemicals. Equal volumes of the two solutions were mixed and stirred. The resulting precipitate was washed with cold distilled water until no chloride ion was detected and vacuum dried 16 h at 110°C.

Sandia-2: solutions of approximately 0.7 M $Zn(NO_3)_2$ and Na_2CrO_4 were prepared. They were mixed in the ratio of 2.5 moles CrO_4^{2-} to 1 mole Zn^{2+}. The precipitate formed was washed, filtered and dried as described for Sandia-1 zinc chromate.

Sandia-3: this material was prepared according to the same procedure as for Sandia-1 except that Na_2CrO_4 was used in place of K_2CrO_4.

Sandia-4: the procedure used to prepare this material was described by Briggs[1]. Dried reagent grade $ZnCO_3$ (4.5 g) was thoroughly mixed with 5.0 ml H_2O. To this mixture 5.0 g dried reagent grade CrO_3 was added. The sample was mixed and heated to remove CO_2. It was sealed in a glass tube and heated 4 h at 208°C. After washing with cold H_2O, the sample was dried at 110°C overnight.

Apparatus and procedures

Thermograms were obtained using a Cahn Vacuum Electrobalance System which included a Model RG electrobalance and a Model 3430 furnace. Temperature was controlled using a Research, Inc. Model 5500/624A Programmer/Controller and measured with a Chromel–Alumel thermocouple suspended inside the hangdown tube. Weight vs. temperature curves were obtained in static room air using heating rates of 1.9, 2.6 and 6.4°C min^{-1}. Relative humidity varied between 10 and 20% and the barometric pressure was in the vicinity of 624 mm Hg. In a few cases weight loss

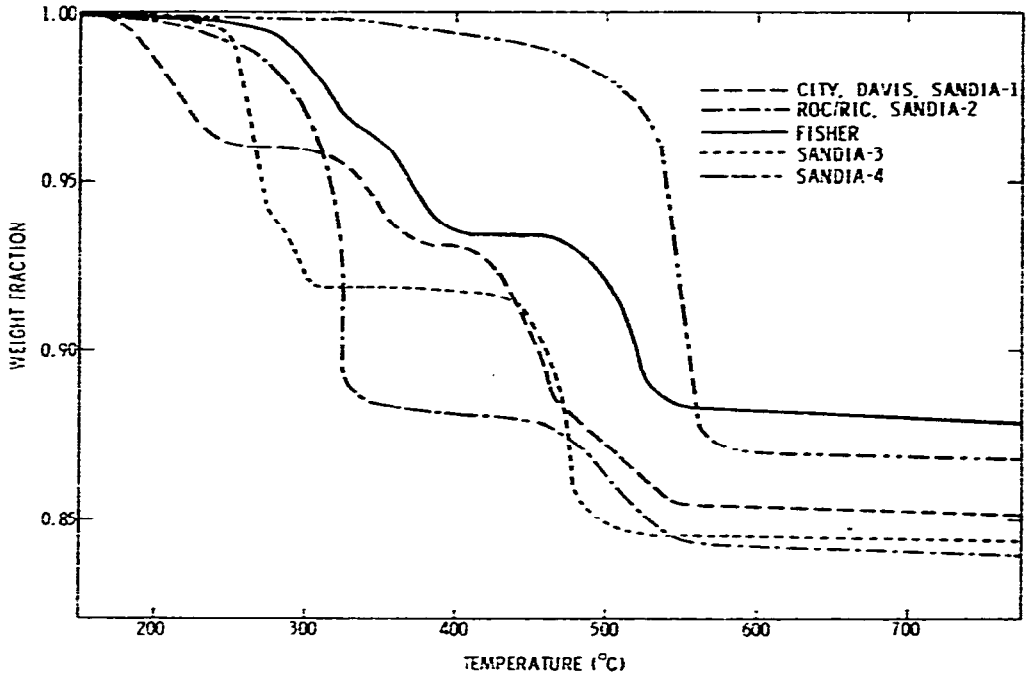

Fig. 1. TG curves for zinc chromates.

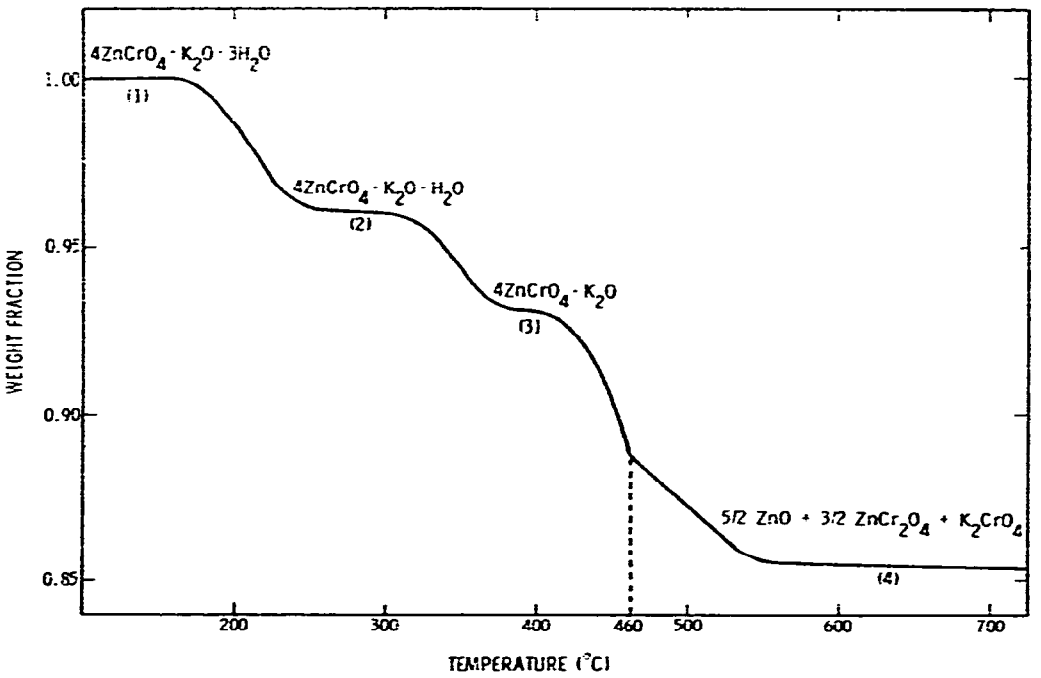

Fig. 2. Thermal decomposition of City, Davis and Sandia-1 zinc chromates.

under isothermal conditions was measured by equilibrating the clamshell type furnace at the desired temperature and then wrapping the furnace around the hangdown tube of the electrobalance. TG samples weighed approximately 15 mg and were contained in flat bottomed platinum pans.

Samples weighing several g were obtained for X-ray, spectrochemical and chemical analyses by heating to equilibrium in an electric furnace at constant temperature. The furnace temperatures were selected on the basis of the thermogram results. In one particular case it was necessary to prepare samples for further analysis by heating them while recording the weight. In this case the heating was continued until a specific point in the thermogram was reached, at which time the heating was stopped and the sample collected.

Chemical analyses consisted of determining chromate content by dissolving the sample in dilute HCl (1.75 N), adding excess KI and titrating the liberated I_2 with 0.1 N $Na_2S_2O_3$ using a starch indicator. Results were reported as weight % $ZnCrO_4$. X-ray analysis consisted of obtaining and analyzing powder diffraction patterns. X-ray powder diffraction and emission spectrochemical analyses were done by conventional techniques.

RESULTS AND DISCUSSION

Thermogravimetry of the eight zinc chromate samples resulted in the five different types of thermogram shown in Fig. 1. The curves for the City Chemical, Davis and Sandia-1 samples were identical. Thermograms for Roc/Ric and Sandia-2 zinc chromates were also the same, while the results for the Fisher, the Sandia-3 and the Sandia-4 samples were each unique. The curves for all samples were independent of heating rate over the range of rates employed.

City, Davis and Sandia-1 zinc chromates

The thermal decomposition scheme for the City, Davis and Sandia-1 materials is shown in Fig. 2. X-ray diffraction patterns at plateaus (1), (2) and (3) were identical and corresponded to $4ZnCrO_4 \cdot K_2O \cdot 3H_2O$. The compounds $4ZnCrO_4 \cdot K_2O \cdot H_2O$ and $4ZnCrO_4 \cdot K_2O$ can also correspond to the same diffraction pattern since waters of hydration can be lost from a compound without changing the *d* spacings of the crystal[2]. The X-ray pattern for the material formed at plateau (4) showed all the major lines for ZnO and for $ZnCr_2O_4$ plus a few of the very strongest lines for K_2CrO_4. No extraneous lines were observed. Semi-quantitative spectrochemical evidence indicated the concentration of the various metallic elements in the samples and agreed with the X-ray results. The final data to support the decomposition scheme shown in Fig. 2 are the results of the chemical analyses. These results along with the weight loss values are shown in Table 2 and compared with the theoretical values based on the proposed reactions. The agreement is quite good.

Additional tests were needed to explain the inflection point observed at ~460°C. This phenomenon can be understood in terms of the following reactions

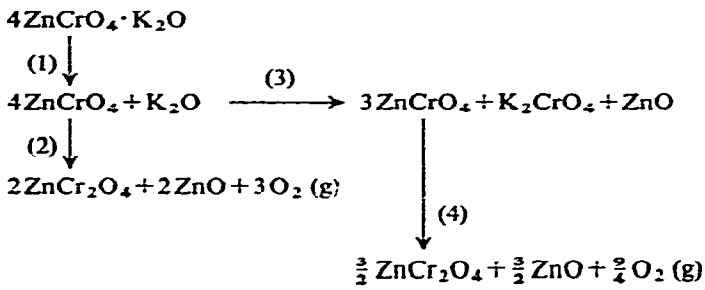

TABLE 2

ASSAY AND WEIGHT LOSS DATA FOR THE THERMAL DECOMPOSITION OF CITY, DAVIS AND SANDIA-I ZINC CHROMATES

Plateau	*Material*	*Temperature (°C)*	*Assay (% $ZnCrO_4$)*		*Weight loss (wt. %)*	
			Theory	*Actual*	*Theory*	*Actual*
1	$4ZnCrO_4 \cdot K_2O \cdot 3H_2O$	<210	83.0	81.0 (C) 79.9 (D) 80.7 (S)	0	0
2	$4ZnCrO_4 \cdot K_2O \cdot H_2O$	210–340	86.6	83.7 (C) 81.6 (D) 83.5 (S)	4.3	3.6 (C) 4.3 (D) 4.3 (S)
3	$4ZnCrO_4 \cdot K_2O$	340–475	88.5	85.3 (C) 82.2 (D) 85.6 (S)	6.2	6.5 (C) 7.1 (D) 6.8 (S)
4	$\frac{5}{2}ZnO+\frac{3}{2}ZnCr_2O_4+K_2CrO_4$	>475	24.3	24.1 (C) 21.3 (D) 23.9 (S)	14.4	14.1 (C) 14.7 (D) 14.7 (S)

TABLE 3

TOTAL PERCENT WEIGHT LOSS FOR DAVIS ZINC CHROMATE HEATED UNDER ISOTHERMAL CONDITIONS

Temperature (°C)	*% Weight loss*
430	14.31
471	14.21
491	14.10
527	13.90

During the decomposition of $4ZnCrO_4 \cdot K_2O$ represented by the curve below 460 °C reactions (1) and (2) are prevalent. At temperatures above 460 °C, reaction (3) begins to become important. This reaction removes some of the chromate radical from the decomposition process since K_2CrO_4 is stable at these temperatures. Consequently, the rate of weight loss is slowed. The results of two experiments support this hypothesis. First, X-ray diffraction analyses on material decomposed to the inflection point showed that $ZnCr_2O_4$, ZnO and possibly $ZnCrO_4$ and/or $4ZnCrO_4 \cdot$

K_2O were present and, significantly, K_2CrO_4 was not present. Secondly, isothermal decompositions were conducted at temperatures slightly below and slightly above the 460°C inflection point. If the proposed scheme is valid, one would expect a larger weight loss at the lower temperatures than at the higher. The results shown in Table 3 support this expectation.

Roc/Ric and Sandia-2 zinc chromates

The steps in the thermal decomposition of the Roc/Ric and Sandia-2 zinc chromates are shown in Fig. 3. X-ray diffraction patterns positively identified the materials listed at the three plateaus, and no unaccounted for lines were noted on the patterns. Emission spectroscopy data supported the X-ray analysis. Table 4 shows the results of chemical analyses and weight loss measurements from the TG. Comparison with theoretical values shows good agreement and supports the proposed decomposition process.

TABLE 4

ASSAY AND WEIGHT LOSS DATA FOR THE THERMAL DECOMPOSITION OF ROC/RIC AND SANDIA-2 ZINC CHROMATE

Plateau	*Material*	*Temperature (°C)*	*Assay (% $ZnCrO_4$)*		*Weight loss (wt. %)*	
			Theory	*Actual*	*Theory*	*Actual*
1	$4ZnO \cdot CrO_3 \cdot 3H_2O$	<320	37.8	41.3 (R) 41.1 (S)	0	0
2	$3ZnO + ZnCrO_4$	320–510	42.6	45.5 (R) 43.8 (S)	11.3	11.0 (R) 13.1 (S)
3	$\frac{7}{2}ZnO + \frac{1}{2}ZnCr_2O_4$	>510	0	2.2 (R) 1.0 (S)	16.3	15.5 (R) 17.4 (S)

Fisher zinc chromate

The Fisher zinc chromate decomposition scheme is shown in Fig. 4. X-ray analysis showed this sample is a mixture of $2ZnO \cdot CrO_3 \cdot H_2O$, $4ZnO \cdot CrO_3 \cdot 3H_2O$ and ZnO. At plateau (2) only the patterns for $2ZnO \cdot CrO_3 \cdot H_2O$ and ZnO were positively identified. At plateau (3) all the lines corresponded to patterns for ZnO and $ZnCrO_4$ and at plateau (4) only ZnO and $ZnCr_2O_4$ lines appeared. Again, spectrochemical evidence supported the interpretation of X-ray patterns.

The percentages of the individual constituents in the undecomposed mixture were determined from chemical analysis and weight loss (TG) data. Based on the calculated composition of 45% $2ZnO \cdot CrO_3 \cdot H_2O$, 30% $4ZnO \cdot CrO_3 \cdot 3H_2O$ and 25% ZnO, the agreement between actual and theoretical % $ZnCrO_4$ and % weight loss is excellent, as seen in Table 5.

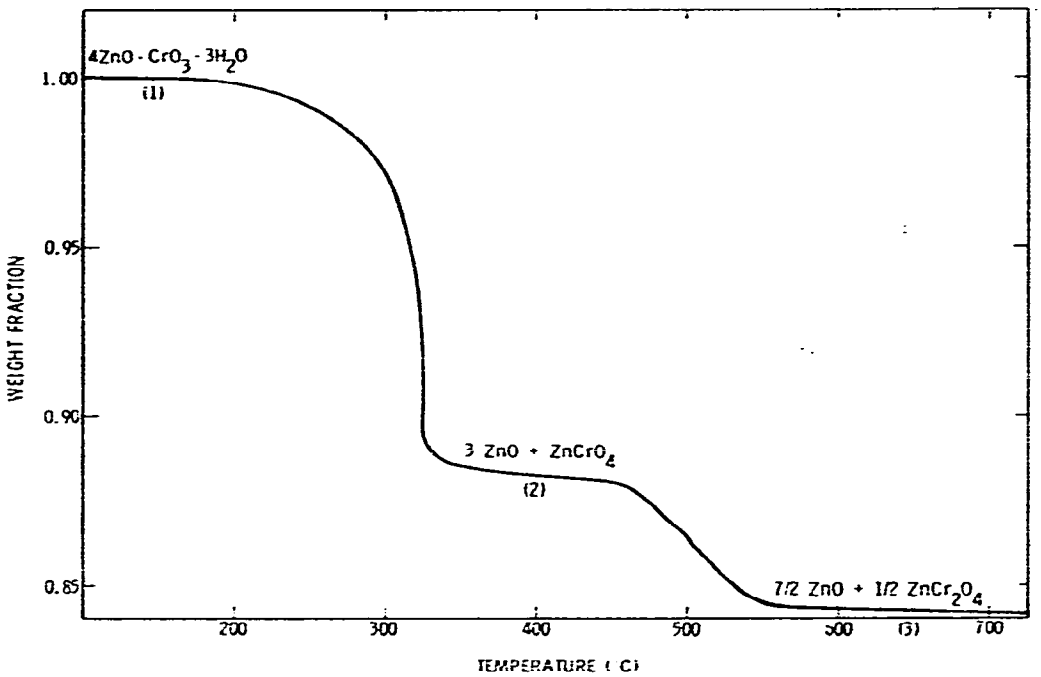

Fig. 3. Thermal decomposition of Roc/Ric and Sandia-2 zinc chromates.

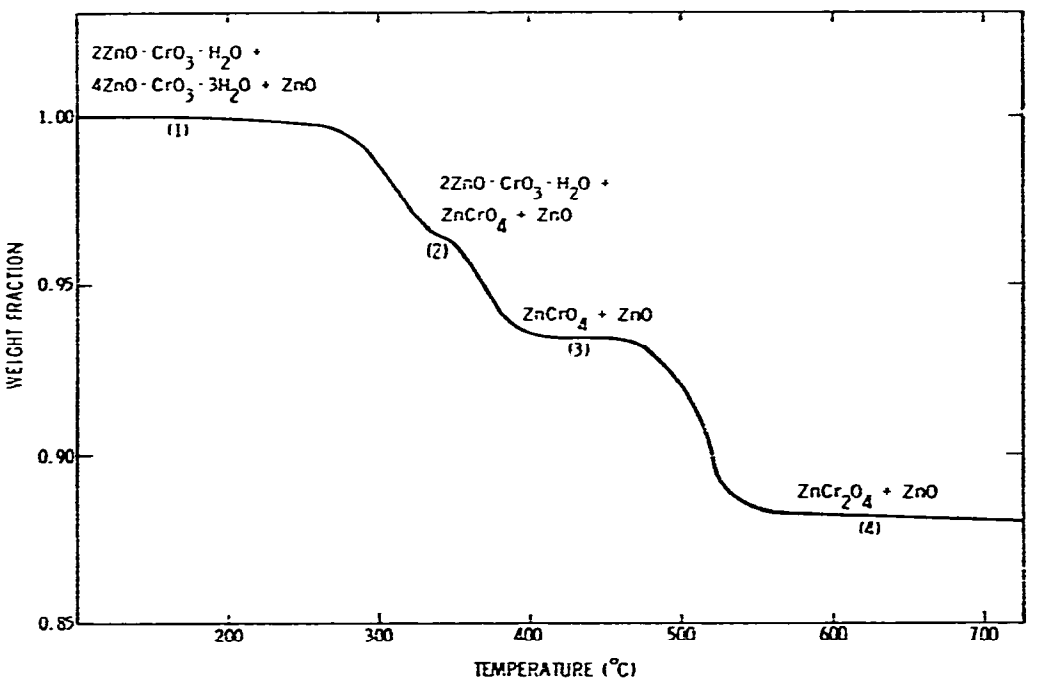

Fig. 4. Thermal decomposition of Fisher zinc chromate.

TABLE 5

ASSAY AND WEIGHT LOSS DATA FOR THE THERMAL DECOMPOSITION OF FISHER ZINC CHROMATE

Plateau	*Material*	*Temperature (°C)*	*Assay (% $ZnCrO_4$)*		*Weight loss (%)*	
			Theory	*Actual*	*Theory*	*Actual*
1	45% $2ZnO \cdot CrO_3 \cdot H_2O$ 30% $4ZnO \cdot CrO_3 \cdot 3H_2O$ 25% ZnO	<300	40.6	40.2	0	0
2	$2ZnO \cdot CrO_3 \cdot H_2O$ $ZnCrO_4$ ZnO	300–370	42.0	40.7	3.8	3.8
3	$ZnCrO_4$ ZnO	370–510	43.3	42.0	6.7	6.7
4	$ZnCr_2O_4$ ZnO	>510	0	0.8	12.1	11.9

Sandia-3 zinc chromate

Working out a decomposition process for Sandia-3 zinc chromate was more difficult because the rather complex X-ray powder diffraction pattern obtained with the starting material could not be interpreted. The tentative decomposition path is shown in Fig. 5. X-ray analysis did, however, identify the compounds shown at plateaus (3) and (4). There were other unidentified diffraction lines for (3) which are probably caused by dehydrated complex compounds of the type $X ZnO \cdot Y CrO_3 \cdot Z Na_2O$. Spectrochemical evidence supported the X-ray results for plateaus (3) and (4).

The starting materials and percentages calculated (35 wt. % $5ZnO \cdot 5CrO_3 \cdot Na_2O \cdot 3H_2O$ and 65 wt. % $5ZnO \cdot 4CrO_3 \cdot Na_2O \cdot 5H_2O$) are in agreement with the weight loss and chemical analysis results as seen in Table 6. They also agree with the semi-quantitative spectroscopy data which indicated Zn and Cr as major constituents (>10%) and Na present at the 1–10% level. The proposed materials contain 33.3% Zn, 23.1% Cr and 4.7% Na. The method of preparation for Sandia-3 zinc chromate was identical to that for Sandia-1 except that Na_2CrO_4 was used for the former and K_2CrO_4 for the latter. Thus, by analogy it is reasonable to expect compounds containing Na_2O in the crystal lattice. Finally, it should be mentioned that diffraction patterns for comparison with compounds of the type $X ZnO \cdot Y CrO_3 \cdot Z Na_2O$ are not available in the literature.

Sandia-4 zinc chromate

The Sandia-4 zinc chromate decomposition was a very straightforward process as shown in Fig. 6. X-ray diffraction patterns showed only $ZnCrO_4$ in this zinc chromate sample with $ZnCr_2O_4$ and ZnO as the decomposition products. The

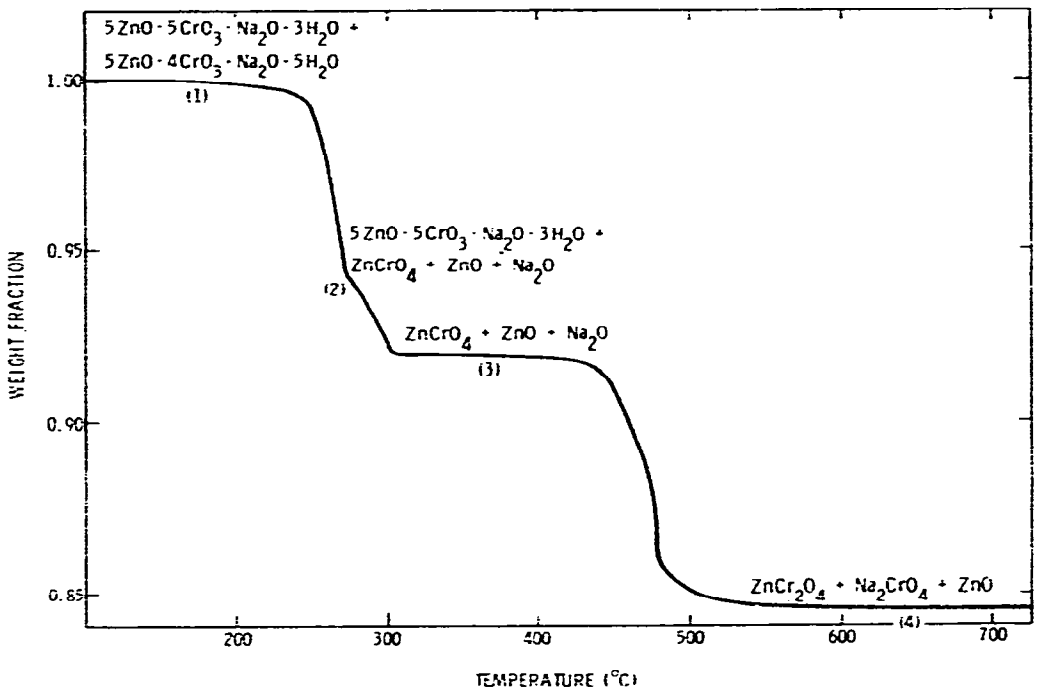

Fig. 5. Thermal decomposition of Sandia-3 zinc chromate.

TABLE 6

ASSAY AND WEIGHT LOSS DATA FOR THE THERMAL DECOMPOSITION OF SANDIA-3 ZINC CHROMATE

Plateau	*Material*	*Temperature (°C)*	*Assay (% $ZnCrO_4$)*		*Weight loss (%)*	
			Theory	*Actual*	*Theory*	*Actual*
1	35% $5ZnO \cdot 5CrO_3 \cdot Na_2O \cdot 3H_2O$ 65% $5ZnO \cdot 4CrO_3 \cdot Na_2O \cdot 5H_2O$	<260	80.2	80.7	0	0
2	$5ZnO \cdot 5CrO_3 \cdot Na_2O \cdot 3H_2O$ $ZnCrO_4$ ZnO Na_2O	260–285	—	—	6.1	5.8
3	$ZnCrO_4$ ZnO Na_2O	285–470	87.0	87.3	8.0	8.2
4	$ZnCr_2O_4$ ZnO Na_2CrO_4	>470	22.1	21.5	16.1	16.2

chemical assay and weight loss data agree well with theoretical values for $ZnCrO_4$ as shown in Table 7. The low assay value of 96.9% is believed to be due to the presence of a small percentage of $2ZnO \cdot CrO_3 \cdot H_2O$. Evidence for the presence of this basic zinc chromate is the small event observed in the TG curve (Fig. 6) at ~355°C. This is about the temperature where the loss of H_2O from $2ZnO \cdot CrO_3 \cdot H_2O$ was previously observed for the Fisher zinc chromate (Fig. 4).

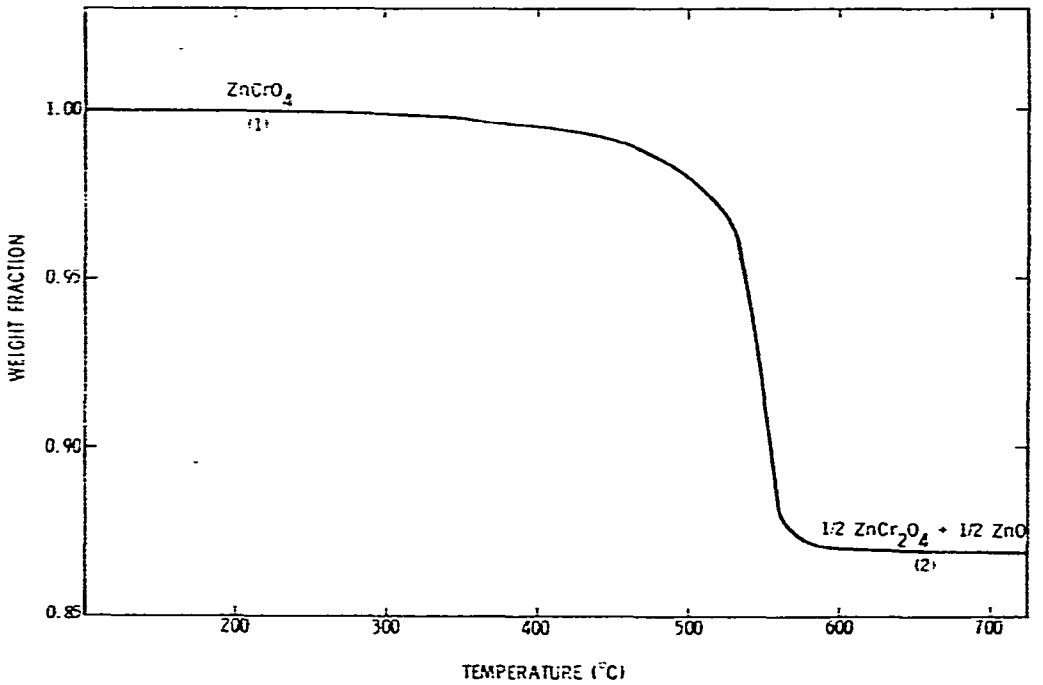

Fig. 6. Thermal decomposition of Sandia-4 zinc chromate.

TABLE 7

ASSAY AND WEIGHT LOSS DATA FOR THE THERMAL DECOMPOSITION OF SANDIA-4 ZINC CHROMATE

Plateau	*Material*	*Temperature (°C)*	*Assay (% $ZnCrO_4$)*		*Weight loss (%)*	
			Theory	*Actual*	*Theory*	*Actual*
1	$ZnCrO_4$	<540	100	96.9	0	0
2	$\frac{1}{2}ZnCr_2O_4 + \frac{1}{2}ZnO$	>540	0	0.2	13.2	13.1

CONCLUSIONS

Decomposition schemes have been postulated for several zinc chromate samples. Excellent agreement was obtained between the proposed processes and the TG, X-ray, spectroscopy and chemical analysis data. It has been shown that "zinc

chromate" may be any of a number of different compounds or mixtures of compounds, with varying chromate content. The compositions of the zinc chromates studied are summarized in Table 8. TG is an excellent method for rapidly distinguishing between these different materials.

TABLE 8
SUMMARY OF ZINC CHROMATE COMPOSITIONS AND ASSAY VALUES

Sample	*Composition*	(% $ZnCrO_4$)
City Davis Sandia-1	$4ZnCrO_4 \cdot K_2O \cdot 3H_2O$	~80.5
Roc/Ric Sandia-2	$4ZnO \cdot CrO_3 \cdot 3H_2O$	~41.2
Fisher	45% $2ZnO \cdot CrO_3 \cdot H_2O$ 30% $4ZnO \cdot CrO_3 \cdot 3H_2O$ 25% ZnO	40.2
Sandia-3	35% $5ZnO \cdot 5CrO_3 \cdot Na_2O \cdot 3H_2O$ 65% $5ZnO \cdot 4CrO_3 \cdot Na_2O \cdot 5H_2O$	80.7
Sandia-4	$ZnCrO_4$	96.9

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