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TR-635

17 September 1958

by

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SPECIFICATION OF PARIUM CHROMATE FOR USE IN GASLESS MIXTURES

TN3-9109
DA-5N05-01-010
DOFL Project 30131

TR-635

17 September 1958

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CONTENTS

	Page
Title	1
Abstract	5
1. INTRODUCTION	5
2. TEST PROCEDURES	6
2.1 Procedures Used for Testing Barium Chromate	6
2.1.1 Chemical Tests	6
2.1.2 Particle Size	7
2.1.3 Mixability	8
2.2 Procedures Used for Testing Heat Mixtures	10
2.2.1 Calorific Value	10
2.2.2 Burning Rate	10
3. RELATIONSHIP BETWEEN BARIUM CHROMATE CHARACTERISTICS AND GASLESS MIXTURE PERFORMANCE	12
3.1 Factors Affecting Gas Evolution	12
Table 1.—ANALYSES OF BARIUM CHROMATE SAMPLES	13
Table 2.—ANALYSES OF BARIUM CHROMATE SAMPLES ARRANGED IN ORDER OF DECREASING MOISTURE	14
Table 3.—ANALYSES OF BARIUM CHROMATE SAMPLES ARRANGED IN ORDER OF DECREASING CARBON DIOXIDE	19
Table 4.—ANALYSES OF BARIUM CHROMATE SAMPLES ARRANGED IN ORDER OF DECREASING TOTAL GAS	24
3.2 Factors Affecting Mixing	29
Table 5.—CHARACTERISTICS OF BARIUM CHROMATE AND ZIRCONIUM-BARIUM CHROMATE MIXTURES	30
3.3 Factors Affecting Calorific Value	35
3.4 Factors Affecting Burning Rate	35
3.5 Factors Affecting Stability	35
4. METHODS OF PREPARING BARIUM CHROMATE	36
4.1 Recommended Reactions	36
4.2 Drying Barium Chromate after Precipitation	36
5. CONCLUSIONS	37
6. RECOMMENDATIONS	38
7. REFERENCES	39

(continued on following page)

C O N T E N T S—Continued

	Page
APPENDICES (cover page)	41
I. CHEMICAL ANALYSIS OF BARIUM CHROMATE	43
1. Chromate	43
2. Barium	43
3. Barium Chromate	43
4. Sulfate	44
5. Chloride	44
6. Sodium and Potassium	44
7. Loss on Ignition at 900°C	44
8. Procedure for the Determination of Moisture and Carbon Dioxide in Barium Chromate	45
8.1 Apparatus	45
8.2 Preparation of Combustion Boats	45
8.3 Preparation of the Barium Chromate Sample	47
8.4 The Determination of Moisture and Carbon Dioxide in the Barium Chromate Sample	47
9. Water-Soluble Matter	48
II. DETERMINATION OF PARTICLE SIZE DISTRIBUTION BY MODIFIED TURBINETRIC METHOD	49
1. Screen Residue	49
2. Preparation of Sample for Turbimetric Particle Size Measurement	49
DISTRIBUTION	51

I L L U S T R A T I O N S

Figure 1. Element, delay (T2E1)	11
Figure 2. Effect of Waring Blender on 20-micron screen residue of barium chromate powder	34
Figure 3. Combustion apparatus for the determination of water and carbon dioxide in barium chromate	46

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ABSTRACT

↓
An investigation was made to determine the relationship between the properties of barium chromate and the characteristics of zirconium heat compositions in which it is used. Thirty-eight samples of barium chromate received from nine suppliers were used in this study. The data show that the gas content of dry barium chromate depends on the total impurities, and does not appear to depend on any individual impurity nor on its surface area; also, that the ability of the barium chromate to blend satisfactorily with zirconium depends on its particle size distribution; and that the calorific values and burning rates of well blended zirconium-barium chromate mixtures with a zirconium content below 35% are not affected by the particle size as long as the size distributions and purity of the barium chromate are within a specified range.

Complete specifications for the procurement of barium chromate suitable for heat powder are included. ↑

1. INTRODUCTION

Barium chromate powder is one of the ingredients used in a number of pyrotechnic delay and heat compositions. These compositions are physical mixtures of one or more metal powders and one or more powdered oxidizing agents that will ignite and react at a predetermined rate upon the application of heat or flame. The combustion of these mixtures is characterized by high reaction temperatures, combustion products that are mainly solids, and the release of very little gas. It should be noted that the oxygen necessary for combustion of the metallic fuel is furnished by decomposition of solid oxidizing agents in the mixture; therefore, no atmospheric oxygen is necessary for combustion.

Only one grade of barium chromate is specified for use in pyrotechnic mixtures. Although the barium chromate described in this specification (ref 1) is suitable for some purposes, it is not completely satisfactory for other applications, particularly those involving heat mixtures. A number of ordnance applications require heat compositions whose properties are controlled closely, and three of these properties are particularly important; (1) extremely low-gas evolution upon combustion, (2) controlled and reproducible heat evolution, and (3) controlled and reproducible burning rate. In addition, safety and other considerations require that the heat compositions be mixed in a

water slurry which requirement imposes certain restrictions on the barium chromate that is used.

However, the relationship between heat powder performance and barium chromate characteristics is not well defined; therefore, this investigation was initiated to: (1) determine the properties of barium chromate that might affect its ability to mix with other ingredients in a water slurry; (2) determine properties of barium chromate that might affect the combustive characteristics of heat mixtures in which it is incorporated; (3) establish simple tests for measuring these properties; and (4) correlate the results of these tests on barium chromate with the performance of heat compositions in which it is used. This investigation is supported by Ord Project TN3-9109.

2. TEST PROCEDURES

Before discussing the results of tests made on barium chromate or mixtures containing barium chromate, it appears advisable to review briefly the test procedures which were used. Analytical and test procedures which are recommended for specification purposes, as well as others which are not readily available in the literature, are detailed in Appendices I and II. The details of the remaining test methods may be found in the appropriate references.

2.1 Procedures Used for Testing Barium Chromate

2.1.1 Chemical Tests^{1/}

Chromate and Barium.—The sample was dissolved in dilute nitric acid, sulfuric acid added, and the chromate titrated potentiometrically with ferrous ammonium sulfate. The solution was then filtered, and the precipitate ignited and weighed as barium sulfate.

Barium Chromate.—The total barium chromate was calculated from the barium and chromate determinations and based on whichever ion had the smaller number of moles per unit weight of sample.

Sulfate.—The material insoluble in dilute hydrochloric acid was ignited and fused with sodium carbonate. The sulfate was precipitated from dilute hydrochloric acid with barium chloride, filtered, ignited, and weighed as barium sulfate.

Chloride.—The chloride was precipitated from dilute nitric acid solution with silver nitrate, dissolved with ammonia, and the solution acidified with nitric acid. The chloride was again precipitated with silver nitrate and weighed as silver chloride.

^{1/} Detailed procedures are in appendix I.

Alkali.—The sample was dissolved with dilute perchloric acid and the determination made with a flame photometer. Readings were taken at 590 millimicrons (mμ) for sodium and 770 mμ for potassium; the readings were compared with standard solutions.

Ignition Loss at 900°C.—The sample was dried to constant weight at 110°C; then the loss on igniting to 900°C was determined.

Soluble Matter (ref 1).—The water soluble matter was determined by boiling the sample for five minutes in distilled water, filtering, and weighing the residue from the evaporated filtrate.

Water and Carbon Dioxide.—A recent investigation (ref 2) has shown that the gases evolved by barium chromate during the combustion of pyrotechnic mixtures are mainly moisture and carbon dioxide. Furthermore, the same data show that many barium chromate samples, although dried to constant weight at 110°C, contain considerable quantities of these gases and that these samples must be heated to elevated temperatures to remove the moisture and carbon dioxide completely. Since pyrotechnic mixtures, particularly heat powder slurries, are usually dried at 110°C or at lower temperatures, it was decided that gas content should be measured only after the barium chromate samples had been dried to constant weight at 110°C.

In the procedure discussed (ref 2), and outlined in appendix I, barium chromate samples are heated to constant weight at 110°C; then heated in a tube furnace at 900°C. A stream of dry argon carries the moisture and carbon dioxide from the sample into adsorption tubes where they are collected and weighed.

2.1.2 Particle Size

The relationships between the particle size of the ingredients of gasless mixtures and the blending and burning characteristics of the mixtures are discussed in detail (ref 3). This reference shows that measurements of both total surface and particle size distribution may be necessary for complete specification of this type of powder. The Brunauer-Emmett-Teller (B.E.T.) method is recommended for total surface measurements; and a modified Eagle-Picher method is recommended for size distribution determinations.

B.E.T. (nitrogen adsorption) Method of Measuring Total Surface (ref 4,5,6).—This procedure depends on removing all adsorbed gas from the surface of the sample; then measuring the quantity of nitrogen necessary to form a monomolecular layer. The total surface area is calculated from this quantity of nitrogen and the cross sectional area of the nitrogen molecule. The apparatus is complicated and requires a skilled operator.

Eagle-Picher Method of Measuring Size Distribution.—This is a turbidimetric method (ref 7) developed by the Eagle-Picher Company to measure the particle size distribution of paint pigments. It uses

a very small sample (2 to 25 milligrams) which is dispersed with a rubber policeman on a watch glass in a small amount of dispersing agent and suspending liquid. The suspension is passed through a 20-micron sieve ^{1/} using a camel's-hair brush and distilled water. The screen is dried and the residue weighed to determine the proportion of the sample larger than 20 microns. The suspension passing through the sieve is diluted to a definite volume and poured into a rectangular cell in the turbidimeter. The change in concentration of the suspension, at a definite level below the surface, with time is measured with a light beam and a photocell. A comparatively small settling distance (1.25 cm) may be used, and this reduces the total time required for settling the suspension to 100 minutes. The calculated particle size distributions are based on the assumption that all particles act as perfect spheres, either when settling or adsorbing light. The calculations for one size distribution measurement require about two hours.

2.1.3 Mixability (ref 8,9)

As mentioned previously, gasless mixtures usually are made by wet blending techniques because of safety considerations. Three wet mixing procedures are in current use. In one method the ingredients are made into a thick paste with water and blended in a muller mixer. It appears probable that the mixing action is a combination of the two types of mixing described below.

In the second method the components are placed in a comparatively dilute water suspension and mixed with a propeller agitator. A small quantity of surface active agent, such as Calgon, is used to aid in dispersing the particles and to allow them to move independently of each other. The success of this method depends on maintaining a completely random dispersal of the particles by agitation. However, it is doubtful if the particles of a mixture can be dispersed evenly throughout a water suspension under these conditions. Each particle of a mixture swirling in a mixing tank will be acted on by several forces. Among these are: (1) the force of gravity; (2) the buoyant force of the suspending liquid; (3) the centrifugal force acting on a particle moving along a curved path; and (4) a drag force which acts to oppose relative motion between the particle and the fluid. The drag force may result from the liquid swirling past the particle during mixing, or it may be caused by the motion of the particle through the liquid under the action of the other forces.

It is important to note that the forces acting on each particle, and the resulting motion, depend on the size and density of the particle as well as the mechanical agitation which is used. The magnitude and direction of the resultant velocity of the particle will

^{1/} Manufactured by Buckbee Mears Co., St. Paul, Minn.

not depend completely on the random influence of the mixing procedure, but will depend also on the size and density of the particle. The net effect will be that particles with different characteristics will tend to separate from each other in the same manner that particles of different sizes or densities would separate in settling tanks and centrifugal separators.

Under these conditions it will be difficult to maintain the same percentage composition of the mixture in all parts of the mixing tank. Theoretically, the tendency of the particles to separate in this manner may be reduced by using ingredients with selected particle size distributions. Practically, it is impossible to obtain the ingredients in sufficiently controlled size ranges to maintain the correct weight ratio of ingredients in all parts of the suspension. In addition, it is difficult to disperse small particles completely in a liquid and any tendency of the particles to agglomerate would change the size distribution. Any lack of control of the size distribution of the ingredients of a blend would cause uneven mixing on a micro if not a macro scale.

The third mixing method, being developed in connection with this investigation (ref 8, 9) depends on using a suspending liquid which tends to agglomerate the components instead of dispersing them. For example, small barium chromate particles tend to form agglomerates, about 20 microns or larger, when they are placed in distilled water; mixtures of zirconium and barium chromate particles agglomerate in distilled water in the same manner. The mixing is accomplished by fluid shear. A Waring Blendor or a Colloid Mill may be used (ref 9) to produce a high-fluid shearing force which will break down agglomerates and allow particles of different materials to mix together. However, as soon as these particles move out of the region of high-fluid shear they immediately reagglomerate and act as particles of gasless mixtures — not as individual components. As a result, there is no tendency of the different components to segregate, and the weight ratio of the components remains constant throughout the blending or subsequent handling operations.

Since the most satisfactory heat powder is produced by this third mixing method, the barium chromate must be tested for its ability to mix in this manner. However, a complete engineering study of the "agglomerate" method of mixing has not been made, and until specified equipment is available on production lines it may be necessary to continue the first two mixing methods on an interim basis. It is believed that barium chromate lots which are suitable for use with the "agglomerate" technique can be used in mixtures made by the first two methods. The suitability of barium chromate produced by a supplier should be tested using small samples and the particular technique being used before large purchases are made.

The "mixability" of barium chromate samples was evaluated by mixing each sample with zirconium powder^{1/} in distilled water

^{1/} Foote Mineral Co. 120A grade zirconium powder.

using a Waring Blendor. The test blends were made with 23.33 grams of barium chromate, 10.00 grams of lot 706-9 zirconium, and 1 liter of distilled water blended at high speed for 20 minutes. The finished mixture was poured into an Imhoff cone and allowed to settle. Under these conditions the forces acting on individual particles tended to separate them. In other words, the heavier particles first sank to the bottom of the cone, followed by lighter particles. Obviously, a barium chromate sample whose particles showed no tendency to separate from the zirconium particles during settling should be satisfactory for making heat mixtures. In some cases it was possible to eliminate some barium chromate samples by visual observation. When no visible segregation of the zirconium and barium chromate occurred samples were removed from the mixture in the cone for chemical analysis. About three grams of the solids were siphoned off the top layer in the cone, the bulk of the solids in the middle layer were removed next, and finally the remaining three grams in the bottom of the cone. The bulk of the sample in the middle layer was reserved for measurements of calorific value and burning rates. The solids in the top and in the bottom layers were dried and used for chromate analyses. The numerical ratio of the chromate content of the bottom layer to the chromate content of the top layer was taken as an indication of the mixability of the barium chromate.

2.2 Procedures Used for Testing Heat Mixtures

Three tests which characterize heat mixtures used in most applications are: calorific value expressed in calories/gram; burning time expressed in millisecond for heat powder tested in a specific manner, and gas evolution expressed as condensable and noncondensable gas evolved by the combustion of one gram of heat powder. Since the gas tester, under development at DOFL, was not available at the time this work was in progress and since data on the contribution of the barium chromate to the total gases were available, it was decided that no attempt would be made to measure the gases evolved during the combustion of heat mixtures. The measurements of calorific value and burning rate are discussed below.

2.2.1 Calorific Value

The calorimetry used for measuring the calorific values of heat mixtures is discussed (ref 10). The apparatus and procedure are similar to that described in ref 11 for the Parr Peroxide Bomb Calorimeter, Model No. 1401. However, a number of modifications have been made in the apparatus and method to adapt them for measuring accurately the calorific values of heat mixtures.

2.2.2 Burning Rate

The burning rates of the heat mixtures were compared by determining the burning time of a definite quantity of each heat mixture loaded into a T2E1 delay element (ref 12) as illustrated in figure 1. The T2E1, which is a standard delay element used in mechanical bomb fuzes for functioning delays in the millisecond range, provided a convenient method for

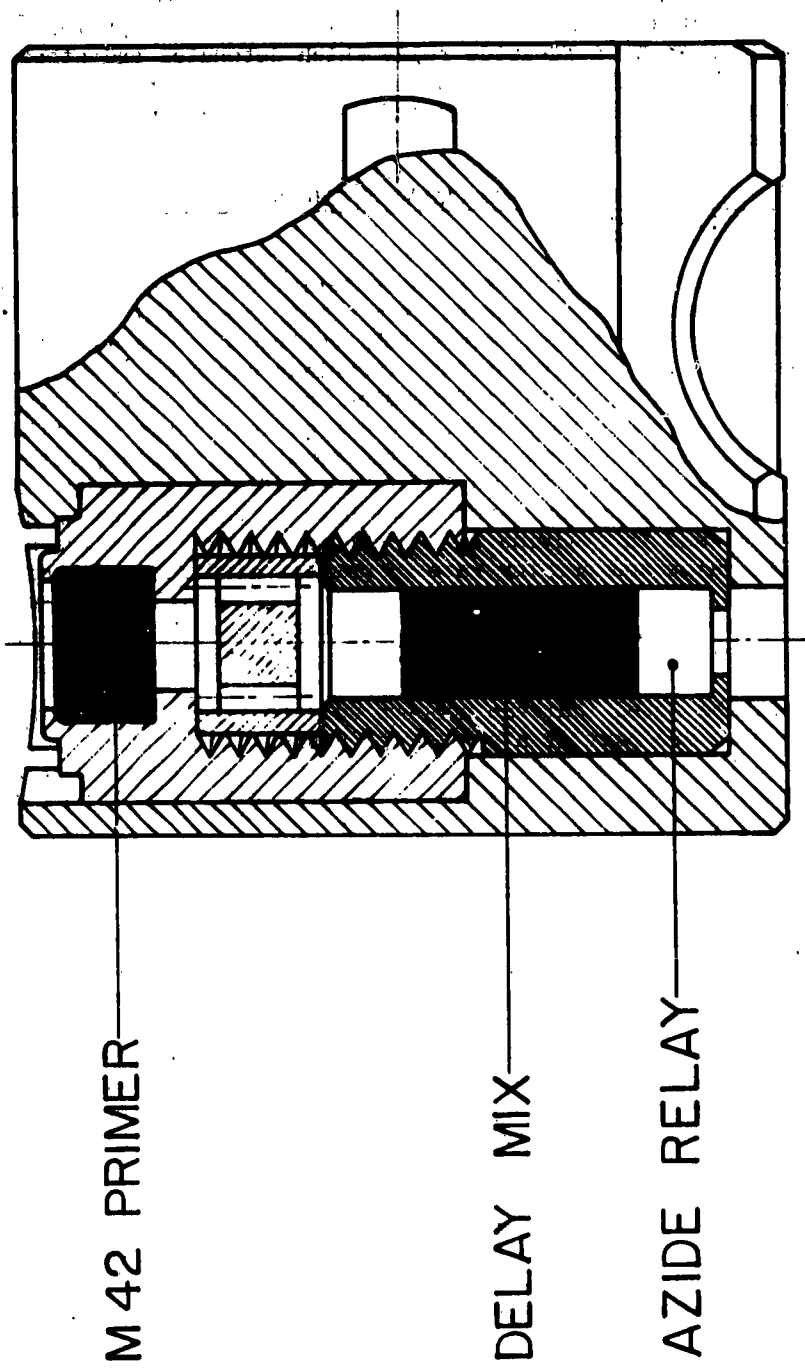


Figure 1.--Element, delay (T2E1).

measuring the burning rate of these mixtures. In this test, 160 milligrams of the heat mixture are pressed at 30,000 psi in a cylinder of 0.125 inch ID. This cylindrical subassembly is inserted in a heavy metal body which acts as a highly efficient heat sink. An eight-megacycle-counter chronograph is actuated when the mix is initiated by M42 primer. The mix burns through to an M6 lead-azide relay which detonates and stops the chronograph. The total elapsed time in millisecon between the initiation of the mix and the explosion of the relay is taken as the burning time of 160 milligrams of the heat mixture.

3. RELATIONSHIP BETWEEN BARIUM CHROMATE CHARACTERISTICS AND GASLESS MIXTURE PERFORMANCE

The effect of barium chromate characteristics on heat powder performance was investigated using samples from eight commercial sources as well as a few experimental samples from a DOFL contractor. Because of limited time and personnel, a "quick sorting" technique was used in this study. The first investigation, made to determine the factors influencing gassing, eliminated samples which would evolve comparatively large quantities of gas during "gasless" reactions. Only the remaining samples, with low gassing qualities, were used in studying factors affecting mixing. Again, only those samples of barium chromate with satisfactory gassing and mixing qualities were used in studying barium chromate characteristics affecting the calorific value and burning rate of gasless mixtures. The effect of only two barium chromate properties—purity and particle size—were considered in this section. The relationship between methods of preparation and barium chromate properties will be considered later.

It should be noted that the numbers used to identify the barium chromate samples are part of a system for designating samples of all materials used in this laboratory. Although the sample numbers used in this report range from 1 to 335, only the 38 samples which are listed were used in this investigation.

3.1 Factors Affecting Gas Evolution

The analytical methods used in this study have been discussed. The chemical analyses and surface measurements were made at the National Bureau of Standards; the moisture and carbon dioxide determinations were made in this laboratory. It should be emphasized that the gas determinations measure only the moisture and carbon dioxide which remain after the sample has been dried to constant weight at 110°C. Since this temperature is the maximum normally used for drying heat mixtures on production lines these tests showed the gases which would remain in the sample after optimum drying.

Effect of Impurities.—The chemical analyses of the barium chromate samples are listed in table 1 with the samples arranged in numerical sequence. The same data, with samples arranged in different sequence, are listed in tables 2, 3, and 4. Table 2—according to decreasing moisture

Table 1.—ANALYSES OF BARIUM CHROMATE SAMPLES

Sample No.	Manufacturer	% CrO_3	% Ba^{++}	% SO_4^{--}	% Cl^-	% Na^+	% K^+	% CO_2	% H_2O	Total Surface B.E.T. Method cm^2/gm	Ignition Loss at 900°C	
1	A	44.8	54.0	0.30	0.31	0.11	0.00	0.16	0.51	-	-	
2	A	44.3	54.3	0.29	0.48	0.02	0.00	0.08	0.54	19,200	-	
3	A	44.5	53.7	0.41	0.50	0.12	0.00	0.04	0.61	47,000	-	
4	B	44.3	53.7	0.32	0.18	0.11	0.00	0.62	0.59	-	-	
5	B	44.7	53.8	0.36	0.21	0.15	0.00	0.14	0.62	-	-	
6	C	44.6	54.3	0.55	0.11	0.02	0.00	0.15	0.27	-	-	
7	C	45.2	54.2	0.05	0.21	0.01	0.00	0.02	0.31	12,300	-	
8	C	44.8	54.2	0.38	0.21	0.02	0.00	0.05	0.36	-	-	
9	E	45.2	53.9	0.06	0.08	0.04	0.23	0.12	0.16	-	-	
10	D	45.7	54.2	0.00	0.02	0.31	0.11	0.01	0.07	-	-	
11	E	45.1	54.4	0.23	0.03	0.01	0.00	0.12	0.11	-	-	
12	F	44.9	54.4	0.22	0.00	0.03	0.00	0.20	0.17	-	-	
13	G	45.2	54.3	0.04	0.00	0.01	0.00	0.16	0.28	-	-	
15	F	45.6	53.7	0.14	0.00	0.01	0.60	0.01	0.42	-	-	
16	F	45.1	54.2	0.24	0.20	0.08	0.00	0.02	0.20	-	-	
23	D	45.7	53.9	0.02	0.06	0.01	0.22	0.01	0.15	27,600	0.26	
30	D	45.7	53.9	0.02	0.06	0.02	0.21	0.01	0.16	-	-	
97	H	45.7	54.2	0.06	0.04	0.01	0.03	0.00	0.06	7,200	-	
98	H	45.7	54.3	0.09	0.01	0.02	0.03	0.00	0.01	3,400	-	
130	H	45.7	54.2	0.13	0.02	0.01	0.00	0.01	0.09	22,800	0.12	
131	H	45.4	53.9	0.00	0.00	0.01	0.00	0.03	0.55	56,600	0.54	
144	I	BaCrO ₄ = 99.3% Impurities not determined							0.08	0.40	57,000	0.44
147	B	45.3	54.1	0.14	0.06	0.04	0.01	0.08	0.18	18,600	-	
150	A	44.8	53.8	0.27	0.42	0.10	0.02	0.08	0.63	44,600	-	
152	A	45.1	53.9	0.28	0.27	0.08	0.01	0.09	0.46	39,300	-	
153	A	44.5	54.7	0.16	0.33	0.10	0.01	0.07	0.69	57,700	-	
154	A	44.9	53.9	0.17	0.25	0.08	0.01	0.07	0.54	39,400	-	
293	D	45.7	54.2	0.00	0.07	0.01	0.16	0.03	0.13	16,600	-	
294	D	45.7	54.1	0.00	0.07	0.01	0.19	0.03	0.14	18,800	-	
296	D	45.3	54.3	0.00	0.30	0.01	0.00	0.04	0.21	5,800	-	
308	D	45.7	54.2	0.00	0.07	0.01	0.16	0.01	0.03	3,300	-	
309	D	45.7	54.1	0.00	0.07	0.01	0.19	0.01	0.03	4,600	-	
313	D	45.7	54.2	0.00	0.07	0.01	0.16	0.03	0.13	16,600	0.23	
314	D	45.7	54.1	0.00	0.07	0.01	0.19	0.03	0.14	18,800	0.20	
317	H	45.4	53.9	0.00	0.00	0.01	0.00	0.01	0.05	45,600	0.06	
325	I	BaCrO ₄ = 99.3% Impurities not determined							0.04	0.05	-	0.09
334	H	45.4	53.9	0.00	0.00	0.01	0.00	0.00	0.00	-	-	
335	I	BaCrO ₄ = 99.3% Impurities not determined							0.00	0.00	-	-

Table 2.--ANALYSES OF BARIUM CHROMATE SAMPLES ARRANGED IN ORDER OF DECREASING MOISTURE

Sample No.	153	150	5	3.	131	4	2	154
<u>Weight Percentage</u>								
H ₂ O	0.69	0.63	0.62	0.61	0.60	0.59	0.54	0.54
CO ₂	0.07	0.08	0.14	0.04	0.01	0.62	0.08	0.07
Total Gas	0.76	0.71	0.76	0.65	0.61	1.21	0.62	0.61
Excess Ba ⁺⁺	2.01	0.76	0.88	1.01	0.15	1.25	1.85	0.74
Excess CrO ₄ ⁼	-	-	-	-	-	-	-	-
SO ₄ ⁼	0.16	0.27	0.36	0.41	0.00	0.32	0.29	0.17
Cl ⁻	0.33	0.42	0.21	0.30	0.00	0.18	0.48	0.25
Na ⁺	0.10	0.10	0.15	0.12	0.01	0.11	0.02	0.08
K ⁺	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.01
Total Impurities	3.37	2.28	2.36	2.49	0.77	3.07	3.26	1.86
Total BaCrO ₄	97.19	97.84	97.62	97.19	99.15	96.75	96.75	98.06
Total Surface B.E.T. cm ² /gm	57,700	44,600	-	47,000	56,600	-	19,200	39,400

(continued on following page)

Table 2--Continued

Sample No.	1	152	15	144	8	7	13	6	296
<u>Weight Percentage</u>									
H ₂ O	0.51	0.46	0.42	0.40	0.36	0.31	0.28	0.27	0.21
CO ₂	0.16	0.09	0.01	0.08	0.05	0.02	0.16	0.15	0.04
Total Gas	0.67	0.55	0.43	0.48	0.41	0.33	0.44	0.42	0.25
Excess Ba ⁺⁺	0.96	0.50	-	-	1.16	0.68	0.78	1.49	0.66
Excess CrO ₄ ⁼	-	-	0.25	-	-	-	-	-	-
SO ₄ ⁼	0.30	0.28	0.14	-	0.38	0.05	0.04	0.55	0.00
Cl ⁻	0.31	0.27	0.00	-	0.21	0.21	0.00	0.11	0.30
Na ⁺	0.11	0.08	0.01	-	0.02	0.01	0.01	0.02	0.01
K ⁺	0.00	0.01	-	-	0.00	0.00	0.00	0.00	0.00
Total Impurities	2.35	1.69	0.83	-	2.18	1.28	1.27	2.59	1.22
Total BaCrO ₄	97.84	98.50	99.05	99.3	97.84	98.72	98.72	97.41	98.94
Total Surface B.E.T. cm ² /gm	-	39,300	-	57,000	-	12,500	-	-	5,800

(continued on following page)

Table 2--Continued

Sample No.	16	147	12	30	9	23	294	314
<u>Weight Percentage</u>								
H ₂ O	0.20	0.18	0.17	0.16	0.16	0.15	0.14	0.14
CO ₂	0.02	0.08	0.20	0.01	0.12	0.01	0.03	0.03
Total Gas	0.22	0.26	0.37	0.17	0.28	0.16	0.17	0.17
Excess Ba ⁺⁺	0.80	0.46	1.24	-	0.38	-	-	-
Excess CrO ₄ ⁻	-	-	-	0.18	-	0.18	0.01	0.01
SO ₄ ⁻	0.24	0.14	0.22	0.02	0.06	0.02	0.00	0.00
Cl ⁻	0.20	0.06	0.00	0.06	0.08	0.06	0.07	0.07
Na ⁺	0.08	0.04	0.03	0.02	0.04	0.01	0.01	0.01
K ⁺	0.00	0.01	0.00	0.21	0.23	0.22	0.19	0.19
Total Impurities	1.54	0.97	1.86	0.66	1.07	0.65	0.45	0.45
Total BaCrO ₄	98.50	98.94	98.06	99.42	98.72	99.42	99.79	99.79
Total Surface B.E.T. cm ² /gm	-	18,600	-	-	-	27,600	18,800	18,800

(Continued on following page)

Table 2. --Continued

Sample No.	313	293	11	130	10	97	317
<u>Weight Percentage</u>							
H ₂ O	0.13	0.13	0.11	0.09	0.07	0.06	0.05
CO ₂	0.03	0.03	0.12	0.00	0.01	0.00	0.01
Total Gas	0.16	0.16	0.23	0.09	0.08	0.06	0.06
Excess Ba ⁺⁺	0.09	0.09	1.00	0.09	0.09	0.09	0.15
Excess CrO ₄ ⁼	-	-	-	-	-	-	-
SO ₄ ⁼	0.00	0.00	0.23	0.13	0.00	0.06	0.00
Cl ⁻	0.07	0.07	0.03	0.02	0.02	0.04	0.00
Na ⁺	0.01	0.01	0.01	0.01	0.01	0.01	0.01
K ⁺	0.16	0.16	0.00	0.00	0.11	0.03	0.00
Total Impurities	0.49	0.49	1.50	0.34	0.31	0.29	0.22
Total BaCrO ₄	99.81	99.81	98.50	99.81	99.81	99.81	99.15
Total Surface B.E.T. cm ² /gm	16,600	16,600	-	22,800	-	7,200	45,600

(continued on following page)

Table 2—Continued

Sample No.	325	308	309	98	334	335
<u>Weight Percentage</u>						
H ₂ O	0.05	0.03	0.03	0.01	0.00	0.00
CO ₂	0.04	0.01	0.01	0.00	0.00	0.00
Total Gas	0.09	0.04	0.04	0.01	0.00	0.00
Excess Ba ⁺⁺	-	0.09	-	0.19	0.15	-
Excess CrO ₄ ⁻	-	-	0.01	-	-	-
SO ₄ ⁻	-	0.00	0.00	0.09	0.00	-
Cl ⁻	-	0.07	0.07	0.01	0.00	-
Na ⁺	-	0.01	0.01	0.02	0.01	-
K ⁺	-	0.16	0.19	0.03	0.00	-
Total Impurities	-	0.37	0.32	0.35	0.16	-
Total BaCrO ₄	99.3	99.81	99.79	99.81	99.15	99.3
Total Surface B.E.T. cm ² /gm	-	3,300	4,600	3,400	-	-

Table 3.—ANALYSES OF BARIUM CHROMATE SAMPLES ARRANGED IN ORDER OF DECREASING CARBON DIOXIDE

Sample No.	4	12	13	1	6	5	9	11
<u>Weight Percentage</u>								
H ₂ O	0.59	0.17	0.28	0.51	0.27	0.62	0.16	0.11
CO ₂	0.62	0.20	0.16	0.16	0.15	0.14	0.12	0.12
Total Gas	1.21	0.37	0.44	0.67	0.42	0.76	0.28	0.23
Excess Ba ⁺⁺	1.25	1.24	0.78	0.96	1.49	0.88	0.38	1.00
Excess CrO ₄ ⁼	-	-	-	-	-	-	-	-
SO ₄ ⁼	0.32	0.22	0.04	0.30	0.55	0.36	0.06	0.23
Cl ⁻	0.18	0.00	0.00	0.31	0.11	0.21	0.08	0.03
Na ⁺	0.11	0.03	0.01	0.11	0.02	0.15	0.04	0.01
K ⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.00
Total Impurities	3.07	1.86	1.27	2.35	2.59	2.36	1.07	1.50
Total BaCrO ₄	96.75	98.06	98.72	97.84	97.41	97.62	98.72	98.50
Total Surface B.E.T. cm ² /gm	-	-	-	-	-	-	-	-

(continued on following page)

Table 3.—Continued

Sample No.	152	2	147	150	144	153	154	8
<u>Weight Percentage</u>								
H ₂ O	0.46	0.54	0.18	0.63	0.40	0.69	0.54	0.36
CO ₂	0.09	0.08	0.08	0.08	0.08	0.07	0.07	0.05
Total Gas	0.55	0.62	0.26	0.71	0.48	0.76	0.61	0.41
Excess Ba ⁺⁺	0.50	1.85	0.46	0.76	-	2.01	0.74	1.16
Excess CrO ₄ ⁼	-	-	-	-	-	-	-	-
SO ₄ ⁼	0.28	0.29	0.14	0.27	-	0.16	0.17	0.38
Cl ⁻	0.27	0.48	0.06	0.42	-	0.33	0.25	0.21
Na ⁺	0.08	0.02	0.04	0.10	-	0.10	0.08	0.02
K ⁺	0.01	0.00	0.01	0.02	-	0.01	0.01	0.00
Total Impurities	1.69	3.26	0.97	2.28	-	3.37	1.86	2.18
Total BaCrO ₄	98.50	96.75	98.94	97.84	99.3	97.19	98.06	97.84
Total Surface B.E.T. cm ² /gm	39,300	19,200	18,600	44,600	57,000	57,700	39,400	-

(Continued on following page)

Table 5.—Continued

Sample No.	3	325	296	293	294	313	314	7
<u>Weight Percentage</u>								
H ₂ O	0.61	0.05	0.21	0.13	0.14	0.13	0.14	0.31
CO ₂	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.02
Total Gas	0.65	0.09	0.25	0.16	0.17	0.16	0.17	0.33
Excess Ba ⁺⁺	1.01	-	0.66	0.09	-	0.09	-	0.68
Excess CrO ₄ ⁼	-	-	-	-	0.01	-	0.01	-
SO ₄ ⁼	0.41	-	0.00	0.00	0.00	0.00	0.00	0.05
Cl ⁻	0.30	-	0.30	0.07	0.07	0.07	0.07	0.21
Na ⁺	0.12	-	0.01	0.01	0.01	0.01	0.01	0.01
K ⁺	0.00	-	0.00	0.16	0.19	0.16	0.19	0.00
Total Impurities	2.49	-	1.22	0.49	0.45	0.49	0.45	1.28
Total BaCrO ₄	97.19	99.3	98.94	99.81	99.79	99.81	99.79	98.72
Total Surface B.E.T. cm ² /gm	47,000	-	5,800	16,600	18,800	16,600	18,800	12,500

(continued on following page)

Table 3.—Continued

Sample No.	16	10	23	308	309	317	30
<u>Weight Percentage</u>							
H ₂ O	0.20	0.07	0.15	0.03	0.03	0.05	0.16
CO ₂	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Total Gas	0.22	0.08	0.16	0.04	0.04	0.06	0.17
Excess Ba ⁺⁺	0.80	0.09	-	0.09	-	0.15	-
Excess CrO ₄ ⁼⁼	-	-	0.18	-	0.01	-	0.18
SO ₄ ⁼	0.24	0.00	0.02	0.00	0.00	0.00	0.02
Cl ⁻	0.20	0.02	0.06	0.07	0.07	0.00	0.06
Na ⁺	0.08	0.01	0.01	0.01	0.01	0.01	0.02
K ⁺	0.00	0.11	0.22	0.16	0.19	0.00	0.21
Total Impurities	1.54	0.31	0.65	0.37	0.32	0.22	0.66
Total BaCrO ₄	98.50	99.81	99.42	99.81	99.79	99.15	99.42
Total Surface B.E.T. cm ² /gm	-	-	27,600	3,300	4,600	45,600	-

(continued on following page)

Table 3.—Continued

Sample No.	131	15	97	98	130	334	335
<u>Weight Percentage</u>							
H ₂ O	0.60	0.42	0.06	0.01	0.09	0.00	0.00
CO ₂	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Total Gas	0.61	0.43	0.06	0.01	0.09	0.00	0.00
Excess Ba ⁺⁺	0.15	-	0.09	0.19	0.09	0.15	-
Excess CrO ₄ ⁼	-	0.25	-	-	-	-	-
SO ₄ ⁼	0.00	0.14	0.06	0.09	0.13	0.00	-
Cl ⁻	0.00	0.00	0.04	0.01	0.02	0.00	-
Na ⁺	0.01	0.01	0.01	0.02	0.01	0.01	-
K ⁺	0.00	-	0.03	0.03	0.00	0.00	-
Total Impurities	0.77	0.83	0.29	0.35	0.34	0.16	-
Total BaCrO ₄	99.15	99.05	99.81	99.81	99.81	99.15	99.3
Total Surface B.E.T. cm ² /gm	56,600	-	7,200	3,400	22,800	-	-

Table 4. -- ANALYSES OF BARIUM CHROMATE SAMPLES ARRANGED IN ORDER OF DECREASING TOTAL GAS

Sample No.	4	5	153	150	1	3	2	154
<u>Weight Percentage</u>								
H ₂ O	0.59	0.62	0.69	0.63	0.51	0.61	0.54	0.54
CO ₂	0.62	0.14	0.07	0.08	0.16	0.04	0.08	0.07
Total Gas	1.21	0.76	0.76	0.71	0.67	0.65	0.62	0.61
Excess Ba ⁺⁺	1.25	0.88	2.01	0.76	0.96	1.01	1.85	0.74
Excess CrO ₄ ⁼⁼	-	-	-	-	-	-	-	-
SO ₄ ⁼⁼	0.32	0.36	0.16	0.27	0.30	0.41	0.29	0.17
Cl ⁻	0.18	0.21	0.33	0.42	0.31	0.30	0.48	0.25
Na ⁺	0.11	0.15	0.10	0.10	0.11	0.12	0.02	0.08
K ⁺	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.01
Total Impurities	3.07	2.36	3.37	2.28	2.35	2.49	3.26	1.86
Total BaCrO ₄	96.75	97.62	97.19	97.84	97.84	97.19	96.75	98.06
Total Surface B.E.T. cm ² /gm	-	-	57,700	44,600	-	47,000	19,200	39,400

(continued on following page)

Table 4.—Continued

Sample No.	131	152	144	13	15	6	8	12	7
<u>Weight Percentage</u>									
H ₂ O	0.60	0.46	0.40	0.28	0.42	0.27	0.36	0.17	0.31
CO ₂	0.01	0.09	0.08	0.16	0.01	0.15	0.05	0.20	0.02
Total Gas	0.61	0.55	0.48	0.44	0.43	0.42	0.41	0.37	0.33
Excess Ba ⁺⁺	0.15	0.50	-	0.78	-	1.49	1.16	1.24	0.68
Excess CrO ₄ ⁼	-	-	-	-	0.25	-	-	-	-
SO ₄ ⁼	0.00	0.28	-	0.04	0.14	0.55	0.38	0.22	0.05
Cl ⁻	0.00	0.27	-	0.00	0.00	0.11	0.21	0.00	0.21
Na ⁺	0.01	0.08	-	0.01	0.01	0.02	0.02	0.03	0.01
K ⁺	0.00	0.01	-	0.00	-	0.00	0.00	0.00	0.00
Total Impurities	0.77	1.69	-	1.27	0.83	2.59	2.18	1.86	1.28
Total BaCrO ₄	99.15	98.50	99.3	98.72	99.05	97.41	97.84	98.06	98.72
Total Surface B.E.T. cm ² /gm	56,600	39,300	57,000	-	-	-	-	-	12,500

(continued on following page)

Table 4.—Continued

Sample No.	9	147	296	11	16	30	294	314
<u>Weight Percentage</u>								
H ₂ O	0.16	0.18	0.21	0.11	0.20	0.16	0.14	0.14
CO ₂	0.12	0.08	0.04	0.12	0.02	0.01	0.03	0.03
Total Gas	0.28	0.26	0.25	0.23	0.22	0.17	0.17	0.17
Excess Ba ⁺⁺	0.38	0.46	0.66	1.00	0.80	-	-	-
Excess CrO ₄ ⁼⁼	-	-	-	-	-	0.18	0.01	0.01
SO ₄ ⁼⁼	0.06	0.14	0.00	0.23	0.24	0.02	0.00	0.00
Cl ⁻	0.08	0.06	0.30	0.03	0.20	0.06	0.07	0.07
Na ⁺	0.04	0.04	0.01	0.01	0.08	0.02	0.01	0.01
K ⁺	0.23	0.01	0.00	0.00	0.00	0.21	0.19	0.19
Total Impurities	1.07	0.97	1.22	1.50	1.54	0.66	0.45	0.45
Total BaCrO ₄	98.72	98.94	98.94	98.50	98.50	99.42	99.79	99.79
Total Surface B.E.T. cm ² /gm-	-	18,600	5,800	-	-	-	18,800	18,800

(continued on following page)

Table 4. --Continued

Sample No.	23	293	313	325	10	97
<u>Weight Percentage</u>						
H ₂ O	0.15	0.13	0.13	0.09	0.07	0.06
CO ₂	0.01	0.03	0.03	0.00	0.01	0.00
Total Gas	0.16	0.16	0.16	0.09	0.08	0.06
Excess Ba ⁺⁺	-	0.09	0.09	-	0.09	0.09
Excess CrO ₄ ⁼	0.18	-	-	-	-	-
SO ₄ ⁼	0.02	0.00	0.00	0.13	0.00	0.06
Cl ⁻	0.06	0.07	0.07	0.02	0.02	0.04
Na ⁺	0.01	0.01	0.01	0.01	0.01	0.01
K ⁺	0.22	0.16	0.16	0.00	0.11	0.03
Total Impurities	0.65	0.49	0.49	0.34	0.31	0.29
Total BaCrO ₄	99.42	99.81	99.81	99.81	99.81	99.81
Total Surface B.E.T. cm ² /gm	27,600	16,600	16,600	22,800	-	7,260

(continued on following page)

Table 4.—Continued

Sample No.	317	308	309	98	334	335
<u>Weight Percentage</u>						
H ₂ O	0.05	0.03	0.03	0.01	0.00	0.00
CO ₂	0.01	0.01	0.01	0.00	0.00	0.00
Total Gas	0.06	0.04	0.04	0.01	0.00	0.00
Excess Ba ⁺⁺	0.15	0.09	-	0.19	0.15	-
Excess CrO ₄ ⁻	-	-	0.01	-	-	-
SO ₄ ⁻	0.00	0.00	0.00	0.09	0.00	-
Cl ⁻	0.00	0.07	0.07	0.01	0.00	-
Na ⁺	0.01	0.01	0.01	0.02	0.01	-
K ⁺	0.00	0.16	0.19	0.03	0.00	-
Total Impurities	0.22	0.37	0.32	0.35	0.16	-
Total BaCrO ₄	99.15	99.81	99.79	99.81	99.15	99.3
Total Surface B.E.T. cm ² /gm	45,600	3,300	4,600	3,400	-	-

content; table 3—decreasing carbon dioxide; and table 4—decreasing total gas. In each case, the total barium chromate content was calculated from the barium and chromate analyses, and was based on the limiting ion in each case. The percentage of barium or chromate in excess was determined from these data and the total impurities in a sample were obtained from the sum of the individual impurities. Although no attempt has been made to calculate the impurities on a stoichiometrical basis, the fact that the sum of the total impurities and total barium chromate is close to 100 percent in every case indicates that all major impurities are included in this total.

The data show that there is no correlation between the moisture, carbon dioxide, or total gas, and the percentages of individual impurities in barium chromate. However, the gases in barium chromate do depend on the total impurities in the sample. In general, the gases decrease as the total impurities decrease; also, the data show that only those samples with less than 1.0 percent total impurities had total gas content within acceptable limits. The latter were set arbitrarily at 0 - 0.20 percent total gas. However, it should be noted that a low percentage of total impurities is not the only requirement for obtaining barium chromate with a low-gas content. Samples 131 and 144 each had total impurities below 1.0 percent, but each also had high moisture content that required further processing which will be discussed later.

In view of this discussion, it is recommended that the barium chromate used in heat powder contains a minimum of 99.0 percent barium chromate.

Effect of Particle Size.—The measurements of total surface (tables 2, 3, and 4) show that there is no correlation between surface areas of the samples and their gas content.

Measurement of Gases for Specification Purposes.—The direct measurement of the gases in barium chromate by the method described in ref 2 requires specialized apparatus and techniques. The total gas also may be determined by measuring the loss on ignition at 900°C of samples previously dried at 110°C. Ignition loss tests, appendix 1, were run on selected samples, and the data in table 5 show that this method is satisfactory for routine determinations of the total gas in barium chromate samples. A maximum ignition loss of 0.20 percent is recommended.

3.2 Factors Affecting Mixing

The mixability test discussed on page 9 was used to evaluate the mixing properties of barium chromate samples with a total gas content below 0.20 percent. Three samples in this group (10, 30, and 97), were depleted before mixability tests could be run. Two additional samples with high gas content (131 and 144) were included in these runs as part of a study relating method of preparing barium chromate with its mixability. This will be discussed in Section 4.2.

Table 5.—CHARACTERISTICS OF BARIUM CHROMATE AND ZIRCONIUM-BARIUM CHROMATE MIXTURES

Sample No.	23	98	150	151	154	204	394	708
Mixability ^{1/} Visual Observation	good	poor	good	good	good	good	good	poor
Analysis CrO ₃ Ratio ^{2/}	1.0160	-	1.0041	1.0024	1.0030	1.0048	0.9965	1.069
Calorific Value calories/gram	444.7	-	445.6	444.8	447.5	-	-	-
Burning Time (milliseconds)	-	-	38.73 ^{3/}	-	40.61 ^{4/}	-	-	-
Surface Area B.E.T. cm ² /gm	27,600	3,400	22,800	56,600	77,000	16,600	18,800	3,300
Water Soluble Matter	.03	-	0	0	.01	-	-	-
Total BaCrO ₄	99.42	99.81	99.81	99.15	99.5	99.81	99.79	99.81
Total Gas app. I para. 8	0.16	0.01	0.09	0.61	0.48	0.16	0.17	0.04
Loss on Ignition - 900°C app. I para. 7	0.26	-	0.12	0.54	0.44	-	-	-
Particle Size Distribution cumulative % percentage smaller than (microns diameter)	20.0	96.0	99.5	99.8	96.2	97.0	-	100
	18.0	96.0	99.5	99.8	96.2	97.0	-	100
	14.0	96.0	99.5	99.8	96.2	97.0	-	99.9
	11.0	94.6	98.9	98.1	95.4	97.0	-	95.5
	9.0	95.6	88.2	95.5	94.2	91.1	-	95.5
	7.0	91.9	77.2	95.0	93.1	89.0	-	91.2
	5.0	88.5	56.8	89.4	92.5	87.5	-	80.7
	3.0	86.6	19.2	86.8	90.6	86.5	-	47.4
	1.5	75.8	7.1	72.5	87.2	85.6	-	14.5
	0.75	44.3	2.0	30.1	77.5	79.8	-	4.4

^{1/} Mixture of 30/70 Zr/BaCrO₄.

^{2/} Ratio of CrO₃ in bottom to CrO₃ in top sections in mixability test.

^{3/} Based on average of 5 measurements.

^{4/} Based on average of 20 measurements.

(continued on following page)

Table 5.—Continued

Sample No.	309	313	314	317	325	344	395
Mixability ^{1/} Visual Observation	poor	good	good	good	good	good	good
Analysis CrO ₃ Ratio ^{2/}	-	1.0030	1.0016	1.0017	0.9955	1.0107	0.9981
Calorific Value calories/gram	-	444.5	445.4	446.1	445.5	446.5	444.9
Burning Time ^{3/} (milliseconds)	-	40.19	39.30	-	39.96	39.97	40.14
Surface Area B.E.T. cm ² /gm	4,600	16,600	18,800	45,600	-	-	-
Water Soluble Matter	-	.06	0	.08	0	-	-
Total BaCrO ₄	99.79	99.81	99.79	99.15	99.3	99.15	99.3
Total Gas app. I para. 8	0.04	0.16	0.17	0.06	0.09	0.00	0.00
Loss on Ignition - 900°C app. I para. 7	-	0.23	0.20	0.06	0.09	-	-
Particle Size Distribution cumulative wt percentage smaller than (microns diameter)	20.0	100	99.9	100	99.7	96.9	87.8
	16.0	100	99.9	100	99.7	96.9	87.8
	14.0	100	99.8	99.9	99.7	96.9	87.7
	11.0	98.9	99.0	98.4	99.6	95.5	86.5
	9.0	98.1	98.3	97.2	98.4	94.1	85.5
	7.0	95.0	97.8	96.2	97.4	93.1	84.7
	5.0	84.9	95.4	95.5	96.8	91.5	84.1
	3.0	57.2	89.9	87.5	96.2	89.1	83.2
	1.5	15.5	62.9	45.7	95.9	87.1	81.6
	0.75	4.8	14.0	16.7	88.1	78.0	70.5

^{1/} Mixture of 30/70 Zr/BaCrO₄.^{2/} Ratio of CrO₃ in bottom to CrO₃ in top sections in mixability test.^{3/} Based on average of 5 measurements.

Effect of Impurities.—Since barium chromate must have a high purity to meet gassing requirements, it does not seem probable that the gross impurities in a sample will affect mixing. However, comparatively small quantities of soluble impurities or impurities on the surface of the barium chromate may affect the zeta potential of the particles in a water suspension and, therefore, may have a marked effect on its mixing properties. For this reason, it is recommended that the soluble impurities in a barium chromate sample, measured by the method discussed previously, be limited to a maximum of 0.01 percent. The soluble impurities in a number of samples are shown in table 5. The impurities on the surface of barium chromate probably depend on the method used in its preparation. Although methods of preparing barium chromate will be discussed briefly in section 4, an exhaustive study of its relationship to mixability has not been made. Therefore, it is recommended that the mixability of large lots of barium chromate be tested whenever a new method of preparation is used.

Effect of Particle Size.—The mixability tests (table 5) show that mixes made with 12 of the 15 barium chromate samples were blended thoroughly and did not segregate on standing. The remaining three mixtures segregated as soon as they were poured into the settling cones, and a large proportion of unmixed zirconium particles remained suspended in the water above material that appeared to be mixed satisfactorily. The data in table 5 show that each of the three barium chromate samples which did not mix properly had a low specific surface and comparatively few particles in the smaller size range. It is suggested that the barium chromate surface in each of these mixtures may not have been sufficient to combine with the available zirconium surface and form agglomerates; also, that these barium chromate samples may be satisfactory for use in mixtures requiring lower proportions of zirconium. However, no tests were run to confirm this.

Although the data (table 5) suggests that B.E.T. specific surface measurements may be adequate for predicting the mixability of barium chromate samples, further consideration will show that such tests will not be satisfactory in all cases. The specific surface of a powder is an average value which does not indicate the range of sizes in the powder. A barium chromate sample with an acceptable specific surface may contain large particles that will prevent it from blending properly.

In order to illustrate the effect of large particles on mixing, a mixability test was run using a specially prepared barium chromate sample containing one percent of sample 15 and 99 percent of sample 313. The former was composed mainly of large crystals about 25 - 30 microns in diameter; and the latter was made up of much smaller particles (table 5) which had satisfactory mixing qualities. The special 23.33-gram barium chromate sample was prepared by adding 0.23 gram of sample 15 and 23.10 grams of sample 313 directly to the slurry in the Waring Blendor. This procedure was used to make certain that the correct proportions of the two samples were used in the mixability test. Obviously,

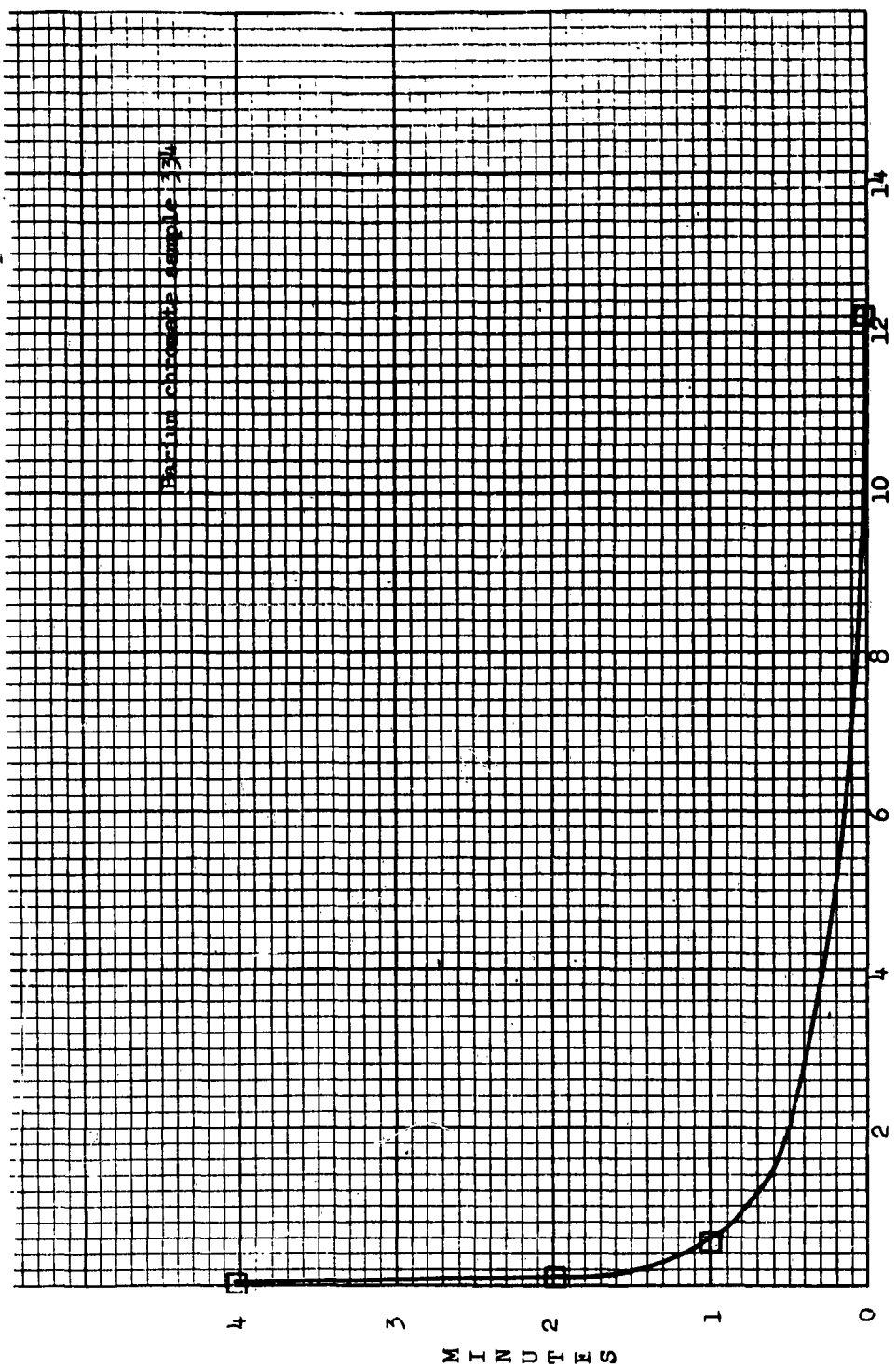
the addition of this quantity of the large barium chromate particles to the much larger amount of sample 313 could change the specific surface of the latter only from 16,600 cm²/gm to a minimum of 16,400 cm²/gm assuming the surface area of the large particles to be negligible. This change in the specific surface is within the limits of accuracy of the B.E.T. test and probably could not be detected readily by this method. However, the mixability test showed that the large barium chromate particles did not blend with the remainder of the sample but fell immediately to the bottom of the mixing cone. It should be noted also that the presence of considerable quantities of large barium chromate particles may not be detected by specific surface measurements if their presence is masked by an abnormally high proportion of fines.

The previous discussion indicates that specific surface measurements are not adequate for determining the mixing qualities of barium chromate samples; also, that the size distribution must be known before the blending properties can be predicted. However, the size distribution data in table 5 is misleading. At first glance the data appear to indicate that satisfactory mixtures can be made with barium chromate samples containing a large proportion of particles larger than 20 microns (μ), but this does not agree with the tests discussed above.

Further investigation showed the apparent discrepancy between tests arose from the different methods used to disperse the samples. In the size distribution test (appendix II) the sample is dispersed by rubbing with a rubber policeman in a sodium pyrophosphate solution on a watch glass, and the particles below 20 μ are passed through a 20- μ sieve using a camel's-hair brush. This method of sample preparation disperses the particles in a reproducible manner with minimum grinding. On the other hand, the Waring Blendor will break down barium chromate particles during the mixability test. The "grinding" action of the Waring Blendor on one barium chromate powder—sample 144—is illustrated in figure 2, where the 20- μ screen residue is plotted against the time the sample is agitated in the blender.

It should be noted that sample 15 did not "grind" or disperse during the mixability test as readily as sample 144. The high specific surface and large proportion of fines in sample 144 suggest that its 20- μ screen residue actually is composed of agglomerates of much smaller particles which break apart with comparative ease, but no further tests were made to confirm this. In any case, the data show that barium chromate samples which contain an appreciable quantity of particles larger than 20 μ may vary in their mixing ability. Therefore, it is recommended that the barium chromate powder contain no more than 0.20 weight percent of particles above 20 μ —measured as the 20- μ screen residue.

The specifications for the minus 20- μ particle size distribution of barium chromate powder are based on the data in table 5 for samples meeting the 20- μ screen residue requirement. Samples which had an excessive proportion of their particles above 20 μ in size were not considered at this time, although they had mixed satisfactorily when broken in the Waring Blendor. The following particle size distribution of barium chromate powder is recommended for specification purposes.



Percentage 20-micron sieve residue

Figure 2.—Effect of Waring Blendor on 20-micron screen residue of barium chromate powder.

Size (microns)	Minimum Cumulative Weight-Percent Undersize	Method of Analysis
20.0	99.8	20- μ screen residue
14.0	99.0	Eagle-Picher Turbidimeter
9.0	97.0	Eagle-Picher Turbidimeter
5.0	95.0	Eagle-Picher Turbidimeter
3.0	87.0	Eagle-Picher Turbidimeter
1.5	50.0	Eagle-Picher Turbidimeter
0.75	16.0	Eagle-Picher Turbidimeter

3.3 Factors Affecting Calorific Value

The data in table 5 show that variations in the purity and particle size of barium chromate samples, which meet the purity and size requirements discussed previously, will not affect the calorific value of zirconium-barium chromate mixtures in which they are used.

3.4 Factors Affecting Burning Rate

The data in table 5 indicate that impurities in barium chromate do not have an appreciable effect on the burning rate of zirconium-barium chromate mixtures in which it is used as long as the purity of the barium chromate is above the requirements previously discussed. However, one impurity, barium sulfate, has been found on the surface of some commercial samples of barium chromate. The sulfate replaces the chromate on the surface of the barium chromate when the latter is washed during the preparation with tap water containing sulfate ion. Since zirconium and barium sulfate are reported to react extremely rapidly in an explosive manner, the presence of barium sulfate on the surface of barium chromate particles is undesirable. Therefore, it is recommended that the sulfate content of barium chromate be held below 0.01 percent.

The data in table 5 show that the particle size distribution of barium chromate samples do not affect the burning rate of thoroughly blended zirconium-barium chromate mixtures as long as the size distribution meets the requirements discussed previously. It is believed that the burning rates of these mixtures do not depend on the barium chromate size distribution, or surface, because the latter is in excess of the zirconium surface; and the agglomerate size of the barium chromate present in the mixtures is larger than the size of the individual barium chromate particles.

3.5 Factors Affecting Stability

No study has been made of the effect of impurities in barium chromate on the storage stability of mixtures in which it is used. However, since the chloride ion generally accelerates the corrosion of metals in

aqueous systems, its concentration is arbitrarily limited to a maximum of 0.05 percent.

4. METHODS OF PREPARING BARIUM CHROMATE

It is believed that barium chromate specifications should require the finished chemical to have definite properties but should place no restrictions on the methods used in preparing it. The processes described below have been used to produce acceptable barium chromate and are intended only as advisory information for organizations interested in barium chromate preparation.

4.1 Recommended Reactions

The most satisfactory reactions for preparing barium chromate for use in heat powder are carried out in water solutions. Reactions run in the solid state have not produced barium chromate suitable for use in heat powders. Although the reactions used for producing the commercial samples discussed in this report are not known, the processes are suggested by the analytical data shown in table 1. The methods of preparing a satisfactory grade of barium chromate are discussed in detail in ref 13. In one of these methods, barium chromate is precipitated from aqueous solutions of barium chloride and potassium chromate in the presence of finely divided alumina (0.1 percent Al_2O_3 based on final dry weight of the product). The properties of this sample (130) and the characteristics of heat mixtures made from this sample are well within acceptable limits. However, the presence of small inert particles during precipitation may not be necessary since commercial samples of barium chromate, presumably prepared without the use of an inert powder, performed as well as sample 130. Reference 13 suggests that the alumina particles act as nuclei for the precipitation of the barium chromate but it may be possible to obtain this same effect by the controlled growth of pure barium chromate crystals.

A second method precipitates barium chromate from aqueous solutions of barium hydroxide and chromic oxide. Samples prepared by this method and dried at $110^{\circ}C$ have a high gas content but the gas can be eliminated by heating them to $700^{\circ}C$. This is discussed in the next section.

4.2 Drying Barium Chromate after Precipitation

Tests were made to determine the advisability of making heat mixtures with barium chromate powder that had been kept in a water slurry without drying after precipitation. Samples 293 and 294 represent barium chromate batches prepared in this manner; samples 313 and 314 represent samples from these batches dried at $110^{\circ}C$. Obviously, the gas content of each pair of these samples was identical since all of them were determined after the samples were dried to constant weight at $110^{\circ}C$. The data in

table 5 show there was no difference in the mixability or burning characteristics of these samples. Since the samples dried at 110°C were satisfactory and since wet barium chromate slurries caused handling difficulties and increased shipping costs, it is recommended that dry barium chromate powder be used in heat mixtures.

Tests also showed that the gas content of barium chromate samples dried at 110°C were not reduced further by vacuum drying at that temperature. Therefore, vacuum drying does not appear to offer any advantages in barium chromate preparation.

An investigation made by the University of Virginia of methods of reducing the gas content of barium chromate showed that the gas could be practically eliminated by heating at 700°C. Samples 97, 131, 144, 293, and 294 were heated for six hours at 700°C. After heating, the respective sample numbers of the heated samples were 98, 317, 325, 308, and 309. The data show that the surface areas of three of the samples (97, 293, and 294) were reduced by sintering, and none produced satisfactory heat mixtures. Two of the samples (131 and 144) produced by the reaction between barium hydroxide and chromic oxide showed very little evidence of sintering and produced heat mixtures that were satisfactory in every respect. Also, satisfactory mixtures were produced from these samples after they had been heated to 900°C for six hours (samples 334 and 335).

It is evident that the best grade of barium chromate for use in heat mixtures is produced by precipitation from barium hydroxide and chromic oxide in an aqueous solution, drying at 110°C or higher, then calcining at 700°C. However, the added expense of preparing barium chromate by this method may not be justified at the present time. Zirconium powder has a hydrogen content of about 0.15 percent by weight and the water resulting from the combustion of this hydrogen is about 0.40 percent based on the weight of the mixture when the zirconium-barium chromate ratio is 30/70. Therefore, the water vapor from the zirconium tends to mask small changes in the moisture content of the barium chromate, and the total gas content of a mixture made with gas-free barium chromate may be only slightly less than when the gas content of the barium chromate is 0.2 percent. However, the use of completely gasless barium chromate may be justified whenever it is necessary to reduce the gas content of a mixture to a minimum or whenever a gasless fuel is available.

5. CONCLUSIONS

The following conclusions apply to barium chromate powder intended for use in zirconium-barium chromate heat mixtures with zirconium powder^{1/} content below 35 percent.

(a) The gas content^{2/} (below one percent) of barium chromate powder depends on its total impurities and not on any individual impurity.

^{1/} Foote Mineral Co. 120A grade zirconium powder.

^{2/} Gas content measured after drying sample to constant weight at 110°C.

(b) The gas content (below one percent) of barium chromate powder does not depend on its surface area.

(c) Barium chromate powder must have a BaCrO_4 content above 99.0 percent to produce an acceptable gas content.

(d) The calorific values and burning rates of zirconium barium chromate mixtures do not depend on the surface areas and size distributions of the barium chromate as long as the size distributions are within specified limits.

(e) The calorific values of zirconium-barium chromate mixtures are not affected appreciably by the purity of the barium chromate if the latter is above 99.0 percent.

(f) Impurities below one percent in barium chromate, with the exception of barium sulfate, do not affect appreciably the burning rate of zirconium-barium chromate mixtures. However, barium sulfate, particularly on the surface of the barium chromate, may increase the burning rate of zirconium-barium chromate mixtures.

(g) The most satisfactory barium chromate for use in heat powders is prepared by precipitation from aqueous barium hydroxide and chromic oxide solutions, followed by drying and calcining at 700°C .

(h) It is possible to manufacture barium chromate powder with a negligible gas content although its use may not be justified at the present time.

(i) The ability of barium chromate powder to mix satisfactorily with zirconium powder depends on its particle size distribution.

(j) The ability of barium chromate powder to mix satisfactorily with zirconium powder may be affected by soluble impurities as well as impurities adsorbed on its surface.

6. RECOMMENDATIONS

The following recommendations apply to barium chromate intended for use in zirconium-barium chromate heat mixtures containing less than 35 percent zirconium.

(a) A mixability test, using both visual observation and chromate analyses of the top and bottom layers, should be run prior to acceptance of large barium chromate lots whenever the supplier or manufacturing methods are changed.

(b) Two grades of barium chromate differing only in volatile matter are specified below:

<u>GRADE 1</u>	<u>GRADE 2</u>
BaCrO ₄ - 99.0 percent minimum	BaCrO ₄ - 99.0 percent minimum
SO ₄ ²⁻ - 0.01 percent maximum	SO ₄ ²⁻ - 0.01 percent maximum
Cl ⁻ - 0.05 percent maximum	Cl ⁻ - 0.05 percent maximum
Volatile matter at 900°C - 0.20 percent maximum	Volatile matter at 900°C - 0.03 percent maximum
Water soluble matter - 0.05 percent maximum	Water soluble matter - 0.05 percent maximum

SIZE DISTRIBUTION
(grades 1 and 2)

Size (microns)	Minimum weight percentage below indicated size	Method of Analysis
20.0	99.8	20-μ screen residue
14.0	99.0	Eagle-Picher Turbidimeter
9.0	97.0	Eagle-Picher Turbidimeter
5.0	95.0	Eagle-Picher Turbidimeter
3.0	87.0	Eagle-Picher Turbidimeter
1.5	50.0	Eagle-Picher Turbidimeter
0.75	16.0	Eagle-Picher Turbidimeter

(c) Grade 1 barium chromate (0.20 maximum percent volatile matter) should be specified unless the gas evolution is sufficiently critical to justify the additional cost of grade 2.

7. REFERENCES

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(continued on following page)

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A P P E N D I C E S

- I. Chemical Analysis of Barium Chromate
- II. Determination of Particle Size Distribution by Modified
Turbimetric Method

CHEMICAL ANALYSIS OF BARIUM CHROMATE1. CHROMATE

Dissolve a 1.0000-gram sample in 100 ml of water and 8 ml HNO_3 (1+1) by warming on a steam bath. Dilute to 200 ml and add 25 ml H_2SO_4 (1+1). Add 4.5000 grams of $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. (This must be a uniform material, standardized against potassium dichromate [NBS standard sample No. 136] by means of this procedure). Dissolve, cool to below room temperature, and titrate the remaining chromate with $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (8 grams per liter) to a potentiometric end point.

Calculation: $A = \% \text{CrO}_4^{=}$

$B = \text{grams } \text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} \text{ used}$

$C = \text{CrO}_4^{=}$ equivalent to 1.000 G $\text{Fe}(\text{NH}_4\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

$D = \text{ml titrating solution used}$

$E = \text{CrO}_4^{=}$ equivalent to 1 ml of titrating solution

$F = \text{weight of sample}$

$$A = 100 \left(\frac{B \times C + D \times E}{F} \right)$$

2. BARIUM

Filter the solution from the chromate determination (section 1, above) through Whatman No. 42 paper; wash well with water. Ignite paper and precipitate in a weighed platinum crucible; cool and add two drops H_2SO_4 . Heat in radiator until fumes cease to be evolved, ignite at 1000°C , cool and weigh as BaSO_4 .

$$\% \text{Ba} = \frac{0.5884 \times \text{wt of } \text{BaSO}_4 \times 100}{\text{wt of sample}}$$

3. BARIUM CHROMATE

Calculate the theoretical barium chromate content from the percentage of barium ion in the sample. Recalculate the theoretical barium chromate content from the percentage of the chromate ion in the sample. Use the lesser of these two values as the actual percentage of barium chromate in the sample.

$$\text{Theoretical } \% \text{BaCrO}_4 = \% \text{Ba}^{++} \times 1.8446$$

$$\text{Theoretical } \% \text{BaCrO}_4 = \% \text{CrO}_4^{=} \times 2.1840$$

APPENDIX I

4. SULFATE

Dissolve a two-gram sample in 150 ml of water and 6 ml of HCl. Filter through Whatman No. 42 paper, washing with HCl (1 + 20), then water. Ignite paper and residue in a platinum crucible; then fuse with one gram of sodium carbonate. Dissolve the melt in water and filter. Make filtrate acid with HCl and add 5 ml of BaCl₂ solution (10%)—let stand overnight. Filter through Carl Schleicher and Schull red ribbon paper, washing with water. Ignite paper and precipitate in a weighed crucible at 1000°C, cool and reweigh as BaSO₄.

$$\% \text{SO}_4 = \frac{0.4114 \times \text{wt of BaSO}_4 \times 100}{\text{wt of sample}}$$

5. CHLORIDE

Dissolve a one-gram sample in 35 ml of water and 5 ml HNO₃ by heating on a steam bath. Add 2 ml AgNO₃ solution (5%). Filter through Whatman No. 42 paper washing with water and discarding filtrate and washings. Dissolve the precipitate by pouring ammonium hydroxide (1+1) through the paper. Reprecipitate the silver chloride by acidifying with HNO₃ (1+1). Filter through a weighed fritted glass crucible, wash with HNO₃ (1 + 100), and dry at 110°C to constant weight, avoiding exposure to strong light which will decompose the precipitate.

$$\% \text{Cl} = \frac{0.2474 \times \text{wt of AgCl} \times 100}{\text{wt of sample}}$$

6. SODIUM AND POTASSIUM

Dissolve 0.2000-g barium chromate in 50 ml of water and 5 ml of perchloric acid by warming on the steam bath. Transfer to a 100-ml volumetric flask and dilute to the mark. Using the Beckman model DU spectrophotometer with flame attachment and photomultiplier, determine the emission at the peaks for sodium (590 mμ) and potassium (770 mμ) correcting the potassium reading for background read at 760 mμ. For sodium, the comparison solutions contain zero, five, and ten ppm sodium oxide in 5% perchloric acid. For potassium, the same concentrations are used, but each also contains 0.2-g barium chromate per 100 ml.

7. LOSS ON IGNITION AT 900°C

Accurately weigh about 5 g of barium chromate into an ignited and weighed porcelain crucible. Heat the crucible and contents at 110°C for two hours. Weigh crucible and contents after desiccator cooling; then heat to 900°C for two hours. Cool in desiccator and reweigh. Express loss of weight on heating to 900°C as percentage loss on ignition.

8. PROCEDURE FOR THE DETERMINATION OF MOISTURE AND CARBON DIOXIDE IN BARIUM CHROMATE (ref 2)

8.1 Apparatus

The combustion train used is shown in figure 3. A drying tower charged with anhydrous magnesium perchlorate follows the argon cylinder. A needle valve is placed in the line to facilitate regulation of gas flow. The gas flow is measured with a Brooks Flowmizer. The Sentry tube furnace is equipped with a Vycor combustion tube. The furnace is operated at a temperature of 1650°F (900°C). The furnace temperature is regulated by a variable input controller. The breech end of the combustion tube is closed by a one-hole rubber stopper with a glass tube through the center to admit the argon. To prevent fine particles of the sample from being blown into the system, a glass wool plug is placed at the tapered exit end of the combustion tube.

A fractional combustion unit charged with silver ribbon is placed in the system following the tube furnace, to react with any chlorine and sulfur compounds which might be present. This unit is operated at a temperature of 707°F (375°C).

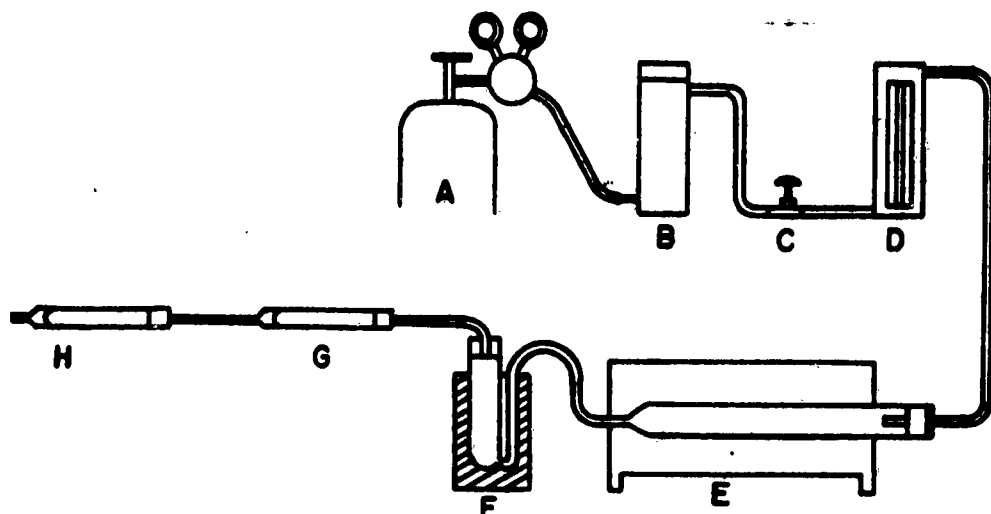
Copper tubing is used for all connections from the argon cylinder to entry into the combustion tube. All other connections are made with pure gum rubber tubing. Micro absorption tubes are used, closed by capillary constrictions. The absorbent for the moisture determination is anhydrous magnesium perchlorate, $Mg(ClO_4)_2$. The carbon dioxide absorption tube is charged with Caroxite, an indicating carbon dioxide absorbent, followed by a small charge of anhydrous magnesium perchlorate.

The complete system is swept with argon at a sweep rate of 125 ml per minute.

8.2 Preparation of Combustion Boats

Coors porcelain combustion boats are used to place the sample into the combustion tube. The boats are cleaned in Calgonite solution, distilled-water rinsed, and predried at 105°C. If barium chromate from a previous run adheres to the boat, it is removed by cleaning with hydrochloric acid before washing in the Calgonite solution. The boats are heated in the tube furnace for 15 minutes at the same temperature and sweep rate at which the samples are to be run. The boats are cooled in air for three minutes and stored in a desiccator until used.

APPENDIX I



- A. CYLINDER OF ARGON WITH REGULATOR
- B. DRYING TOWER PACKED WITH ANHYDROUS MAGNESIUM PERCHLO-
RATE
- C. NEEDLE VALVE
- D. BROOKS FLOWMIZER
- E. COMBUSTION TUBE IN COMBUSTION FURNACE
- F. FRACTIONAL COMBUSTION UNIT CHARGED WITH SILVER RIBBON
- G. MOISTURE ABSORPTION TUBE CHARGED WITH ANHYDROUS
MAGNESIUM PERCHLORATE
- H. CARBON DIOXIDE ABSORPTION TUBE CHARGED WITH CAROXITE
FOLLOWED BY ANHYDROUS MAGNESIUM PERCHLORATE

Figure 3.—Combustion apparatus for the determination of water and carbon dioxide in barium chromate.

8.3 Preparation of the Barium Chromate Sample

- a. Dry at 105°C to constant weight.
- b. Weigh a 5-g sample and transfer into a predried combustion boat.
- c. Dry the sample and the boat at 105°C for one hour.
- d. Transfer directly to combustion furnace and test immediately.

8.4 The Determination of Moisture and Carbon Dioxide in the Barium Chromate Sample

- a. Bring the combustion furnace to operating temperature 1650°F (900°C). Sweep system with argon at the desired flow rate (125 ml per minute) for 20 minutes.
- b. Connect absorption tubes into the system. The moisture absorption tube is placed first in the chain, followed by the carbon dioxide absorption tube.
- c. Sweep absorption tubes for 20 minutes.
- d. Disconnect the absorption tubes and place them in the balance case to cool for 5 minutes. Weigh to get initial weight.
- e. Repeat step b.
- f. Immediately shut off needle valve.
- g. Place a preheated combustion boat into the heat zone of the combustion furnace and restopper the combustion tube.
- h. Open the needle valve and adjust the sweep rate to 125 ml per minute.
- i. Sweep the system for 20 minutes, collecting the blank.
- j. Disconnect the absorption tubes and place them in the balance case to cool for 5 minutes—weigh.

Subtract initial weight (step d of this section) to determine the blank.

- k. Repeat steps b and f of this section.
- l. Place the preheated sample (see sample preparation, section 8.3) into the heat zone of the combustion furnace and restopper the combustion tube.

APPENDIX I

- m. Repeat steps h, i, and j (this section). Calculate the percentage of moisture and carbon dioxide present.

$$\% = \frac{\text{wt gain}}{\text{wt of sample}} \times 100.$$

9. WATER-SOLUBLE MATTER (ref 1)

Prepare wash water for use in this determination as follows: Place a few grams of pure, thoroughly washed barium chromate in a beaker and add 500 ml of water. Heat mixture to the boiling point and allow to boil for 5 minutes. Cool the mixture to room temperature, and filter the solution through a No. 42 Whatman - or equivalent - filter paper, refiltering if necessary to obtain a clear filtrate. Transfer a measured portion of 60 ml of the clear filtrate to a tared 100-ml beaker and evaporate to dryness on a steam bath. The liquid may be evaporated on a hot plate to a volume of approximately 2 ml, if care is taken to prevent mechanical loss and the evaporation then completed on a steam bath. Dry the beaker and contents for one hour in an oven at 100°C to 105°C; cool in a desiccator, and weigh. Subtract the weight of the beaker from that of the beaker and contents to obtain the weight of pure barium chromate soluble in 60 ml of wash water. Transfer a weighed portion of approximately 5 grams of the sample, finely ground, to a 150-ml beaker. Add 50 ml of water saturated with barium chromate, prepared as described above. Cover the beaker with a watch glass, heat the mixture to the boiling point, and allow to boil for 5 minutes. Cool the mixture to room temperature, and filter the solution by decantation through a 7-cm No. 42 Whatman (or equivalent) filter paper, catching the filtrate in a tared 100-ml beaker. Refilter if necessary to obtain a clear solution. Wash the insoluble matter twice with 5-ml portions of the water saturated with barium chromate. Evaporate the combined water extract and washings as described above. Dry the beaker and contents in an oven at 100°C to 105°C for one hour; cool in a desiccator and weigh. Correct for the weight of pure barium chromate soluble in 60 ml of the wash water, and calculate the corrected weight of the residue to percentage of water-soluble matter in the sample.

DETERMINATION OF PARTICLE SIZE DISTRIBUTION BY MODIFIED
TURBIDIMETRIC METHOD

1. SCREEN RESIDUE

A 20- μ sieve^{1/} is placed in a funnel leading to a 400-ml beaker. One (1.000) gram of sample is weighed onto a watch glass, and a few ml of saturated sodium pyrophosphate solution added. The sample is dispersed to a smooth paste with a rubber policeman and washed onto the screen with water from a wash bottle. The suspension is washed through with water containing 20 ml saturated sodium pyrophosphate per liter. A camel's-hair brush is used to assist the transfer. When all the fine material has passed through, the screen and sample are washed with distilled water, then with acetone and air-dried. The residue is transferred to a tared weighing bottle, dried at 110°C, cooled in a desiccator and weighed.

2. PREPARATION OF SAMPLE FOR TURBIDIMETRIC PARTICLE SIZE MEASUREMENT

The sample is weighed (ref 7) onto a watch glass and a drop of the saturated sodium pyrophosphate dispersing agent added. Sample and solution are rubbed with a rubber policeman until thoroughly blended, all aggregates being broken down. The 20- μ screen is placed in a funnel whose stem leads to a 250 ml glass-stoppered graduated cylinder. The balance of the sodium pyrophosphate solution (2.4 ml total) is poured onto the screen and the blended sample washed off the watch glass and policeman with distilled water. If no material larger than 20 μ is present, a wash bottle will suffice to wash the sample through, but if some larger particles are present, a camel's-hair brush should be used to make sure that all particles smaller than 20 μ pass through. The screen is washed thoroughly to remove all particles from the bottom. The funnel is washed and removed and the suspension made up to the proper volume with distilled water. The cylinder is stoppered and shaken to give a uniform suspension which is poured into the apparatus without delay.

If the screen contains a residue, it is washed with acetone, air dried, transferred to a weighing bottle, dried at 110°C and weighed. If this weight is larger than would be expected from the screen residue test, the particle size determination must be repeated on a fresh sample.

^{1/} Manufactured by Buckbee Mears Co., St. Paul, Minn.