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COMPOSITE PROPELLENT CATALYSTS: COPPER CHROMATE AND COPPER CHROMITE

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SUMMARY

The thermal decompositions of copper chromate and copper chromite have been examined by simultaneous thermogravimetric analysis and differential thermal analysis. Decomposition proceeds in successive stages ultimately yielding cuprous chromite and cuprous oxide from both copper chromate and copper chromite.

Alternate successive exposure of the catalyst at 400-420°C to fuel (ammonia, isobutene or ethylene) and oxygen showed that after the initial reduction, a redox cycle occurred between cupric oxide and copper. Both stages of the redox cycle were associated with exothermic reactions. No redox cycle was observed when methane was used as a fuel. When perchloric acid was used as oxidizer, an irreversible weight change occurred, along with the oxidation part of the redox cycle.

The relevance of these results to the mechanism of composite propellent catalysis is discussed.

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1 INTRODUCTION

Modification of the burning rate of composite propellents based on ammonium perchlorate in a matrix of polymeric fuel is frequently achieved by addition of small amounts (about 1% by weight) of various substances. In the U.K. the additive used to increase the burning rate is often copper chromate; in the U.S.A. copper chromite is frequently used.

The mechanism by which such catalysts are effective has long been debated Attempts have been made to elucidate the detailed mechanism by experiments with model mixtures[1,2]. However, the results of such experiments are often ambiguous and the role of the copper-chromium compound is subject to conjecture.

Recent experiments have shown that such catalysts are effective in promoting the ignition of (a) gaseous fuel - perchloric acid vapour[3], (b) solid fuel-perchloric acid vapour[4] and (c) solid fuel - oxygen[5] systems. These experiments[4] also showed that perchloric acid decomposes exothermically on copper chromite catalyst which simultaneously undergoes partial chemical changes[6]. The ability of transition metal oxides to catalyse the decomposition of perchloric acid has been confirmed by Solymosi[7].

In the present work, these copper-chromium compounds are characterised and their behaviour when heated or exposed to various reactive gases is studied. Evidence is presented that a redox cycle is involved in the action of such catalysts in mixtures of gaseous fuel with oxygen or perchloric acid vapour. The results are discussed in relation to the role of such catalysts in the combustion of ammonium perchlorate propellents.

2 EXPERIMENTAL AND TECHNIQUES

2.1 Materials

Two samples of copper chromate and of copper chromite were used. Supplementary experiments were made with cupric oxide. The catalysts and their sources are given in Table 1.

The gaseous reactants were perchloric acid vapour (obtained by vaporization[8] of 72% by weight perchloric acid (Hopkins and Williams Ltd.) ammonia (ICI Ltd.), isobutene (Air Products Corp.), ethylene, oxygen and nitrogen (British Oxygen Co.) and methane (West Middlesex County Council Main Drainage Dept.).

2.2 Techniques

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) experiments were made on the catalyst samples using a nitrogen atmosphere in a Stanton thermobalance type TR-02.

The apparatus previously used to study the ignition of composite propellent fuels[8] was used to study the effect of reactive gases on the catalyst samples. The catalyst was contained in the heated glass tube and the gases introduced through another heated glass tube of smaller diameter.

Temperatures were measured using chromel-alumel thermocouples with a cold junction in ice.

2.3 Analytical methods

The composition of the catalyst samples as supplied was determined as follows:

(i) Copper was determined iodometrically after reduction of chromium with sulphur dioxide, except in the case of RIC copper chromite when the copper was determined by atomic absorption spectrophotometry after solution in perchloric acid.

(ii) Chromium was determined by titration of chromate with ferrous ion.

It was necessary to fuse the copper chromite samples with fusion mixture to dissolve them.

3 RESULTS

Before the chemical mechanism by which these catalysts are effective could be elucidated, it was necessary to characterise the particular samples of 'copper chromate' and 'copper chromite' which are not pure cupric chromate, $CuCrO_4$, or cupric chromite, $CuCr_2O_4$, respectively. This characterisation was made by chemical analysis of the copper and chromium content of each sample and by simultaneous DTA and TGA.

3.1 Catalyst compositions

The chemical analyses for each sample are shown in Table 2. It is possible to derive empirical formulae by assuming that the copper chromate samples are $CuCrO_4.x\ Cu(OH)_2$ and that the copper chromite samples are $CuCr_2O_4.y\ CuO$. This was done graphically by plotting the theoretical percentage compositions of copper and chromium for values of x in $CuCrO_4.x\ Cu(OH)_2$ from 0.5 to 3.0 and of y in $CuCr_2O_4.y\ CuO$ from 0.5 to 10.0. The empirical formulae corresponding to the analytical results are given in Table 2.

3.2 DTA-TGA experiments

Samples of the catalysts were heated at 5 deg C min^{-1} from ambient temperature to 1100°C in a flow of nitrogen (white spot: 0.2 litre min^{-1}). Percentage weight losses calculated from the TGA results are plotted against temperature in Fig.1.

Several weight loss stages are evident which may be identified from the known components of the samples. The stages are thus tentatively assigned to the following processes:

(i) Ambient - 425°C : Loss of water
(ii) 425°C - 525°C : Cupric chromate → cupric chromite
(iii) 700°C - 850°C : Cupric chromite → cuprous chromite
(iv) 875°C - 1000°C : Cupric oxide → cuprous oxide.

The simultaneous DTA results show a series of endotherms and occasionally an exotherm. The positions of the peaks of these heat changes are shown in Table 3.

The endotherms at 470°C, 740-800°C and 950°C may be assigned to the processes (ii), (iii) and (iv) respectively found in the TGA results.

3.3 Reaction with gaseous fuels and oxidants

The effect of passing either a gaseous fuel or a gaseous oxidizer over a heated sample of the catalyst was examined gravimetrically and by recording the temperature change of the sample when the gas was introduced.

3.3.1 Temperature changes

The temperature of the sample was monitored by placing a chromel-alumel thermocouple so that the junction was covered by a layer of catalyst. It is apparent that the temperature changes recorded will depend on the precise position of the thermocouple and the results are therefore qualitative.

The experimental observations for a sample of copper chromate may be summarized as follows:

(i) Methane was not reactive either alone or with oxygen.

(ii) Simultaneous introduction of a fuel (ammonia or isobutene) and oxygen caused the catalyst to glow red hot and a rapid temperature rise was recorded. The glow was sustained as long as the gas mixture was introduced.

(iii) Alternate successive introduction of fuel and oxygen gases produced transient glows and temperature rises. Repeated exposure to a single gas resulted in no marked heat release or visible glows on the second and subsequent exposures.

(iv) Exposure of the sample to ambient air between the introduction of fuel and oxygen caused the temperature rise on introduction of the oxygen to be reduced.

(v) The temperature rise was greatest on the first introduction of fuel vapour to a fresh sample of catalyst.

(vi) Subsequent exposure to fuel and oxygen is ineffective at 260-270°C unless the catalyst is reactivated by heating to about 500°C, e.g. by simultaneous introduction of fuel and oxygen.

(vii) At higher temperatures, about 400°C, the temperature rise is greater for isobutene than for ammonia, which is greater than for ethylene. On the other hand, the temperature rise on the subsequent introduction of oxygen is similar for each of these fuel gases.

Harshaw copper chromite behaved in a similar way except that the temperature rise is greatest for ethylene and least for ammonia.

3.3.2 Gravimetric results

The temperature changes showed that copper chromate and copper chromite reacted rapidly above 350°C with gaseous fuels (ammonia, isobutene and ethylene) and oxygen when these were introduced alternately. Several modes of reaction are possible:

(i) Activation of fuel molecules by adsorption on the surface of the catalyst (no interaction with the oxygen in the catalyst) followed by subsequent reaction with oxygen gas.

(ii) Reaction of fuel molecules with catalyst oxygen in the surface layer, followed by replacement of the catalyst oxygen from the gaseous oxygen.

(iii) Reaction of fuel molecules with catalyst oxygen throughout the bulk of the catalyst.

The changes in weight of samples of catalyst were determined to distinguish between processes (i) and (ii) or (iii). Different sample weights were used to distinguish between surface (ii) and bulk reaction (iii).

The gravimetric experiments were all made at 400-420°C and followed a standard pattern. Samples of the catalyst, as supplied, were first heated to determine the water content. They were then exposed to fuel and oxidizer gases alternately.

The percentage weight losses and gains observed for copper chromate and copper chromite in ammonia, isobutene, ethylene, methane or oxygen are shown in Fig.2. Methane was found to be unreactive thus confirming the observation that no temperature change occurred on exposure to the gas. Although sample weights of chromate and chromite of 0.16-0.46 and 0.37-0.97 gram respectively were used, the reproducibility was good and the percentage weight changes were independent of sample weight thus showing that a bulk reaction was involved. Further, the percentage weight losses were independent of the nature of the fuel (ammonia, isobutene or ethylene) showing that reduction of the catalyst was involved rather than an adsorption process in which adsorbed fuel molecules were subsequently oxidized.

A more extensive series of experiments in which duplicate samples of each catalyst were used and which included perchloric acid as an oxidizer are shown in Fig.3. The reproducibility was observed to deteriorate after the samples had been exposed to perchloric acid vapour, suggesting that surface reaction as opposed to bulk reaction had occurred. This was confirmed by visual observation and by the dependence of the percentage weight change on sample weight shown in Fig.4. The surface layer of the chromate and chromite samples changed colour from black to a mottled reddish-brown on exposure to perchloric acid, and an alkaline extract of the modified sample was yellow indicating chromate ion. No such chromate formation was observed on exposure to oxygen.

The cupric oxide samples were effectively de-activated by exposure to perchloric acid vapour because the percentage weight changes after acid attack were reduced by a factor of 5 or 6 from those previously recorded. The cupric oxide samples were also observed to reduce the amount of perchloric acid fumes, presumably by catalysing the decomposition of the acid vapour. No parallel effect was observed with the chromate-chromite samples, which suggests that cupric oxide is a more effective catalyst for the decomposition of perchloric acid vapour.

4 DISCUSSION

4.1 Thermal decomposition of copper chromate and copper chromite

In addition to use as a ballistic modifier for solid propellents, copper chromite has wide commercial application as a catalyst, for example, in automobile exhaust systems[9] in which it is used to achieve complete oxidation of carbon monoxide and of hydrocarbons to carbon dioxide. Consequently, the nature of the chemical compounds in copper chromite catalyst and the effect thereon of heat have been studied.

An early study[10] showed that cupric chromite-cupric oxide mixtures were converted to cuprous chromite on heating at about 900°C:

$$CuCr_2O_4 + CuO \rightarrow Cu_2Cr_2O_4 + \tfrac{1}{2}O_2 \quad . \qquad (1)$$

The cuprous chromite produced was stated to be stable at room temperature but reaction (1) could be completely reversed by heating in oxygen for several hours at 600-700°C. Pure cupric chromite decomposed at temperatures above 900°C to cuprous chromite and chromic oxide:

$$2CuCr_2O_4 \rightarrow Cu_2Cr_2O_4 + Cr_2O_3 + \tfrac{1}{2}O_2 \quad . \qquad (2)$$

Reactants and products in both these reactions were identified by X-ray diffraction.

More recently, the CuO-Cr_2O_3-copper chromite system has been examined by Charcosset et al[11,12] using DTA and analytical methods. DTA of a cupric oxide-chromic oxide mixture showed an exotherm at 375°C followed by an endotherm at about 500°C. Analysis at 425°C showed that chromate was present and it was concluded that the exotherm corresponded to crystallization of the chromic oxide (initially in the amorphous state) and formation of copper chromate. The endotherm was assigned to the decomposition of the chromate to chromite and this was confirmed by DTA of a sample of copper chromate. X-ray analysis of the CuO-Cr_2O_3 sample above 800°C showed that the cupric chromite had been converted to cuprous chromite confirming the earlier observations[10].

A kinetic study showed that cupric chromite was not obtained from a CuO-Cr_2O_3 mixture below 550°C even on heating for 24 hours. However, the addition of 10% cupric chromite reduced the limiting temperature to below 410°C. Thermogravimetric studies of copper chromate at constant temperature showed that decomposition occurred at measurable rates at 400-450°C. The reaction is initially fast but then slows down before accelerating again, showing that autocatalysis is involved after the initial reaction. Chemical and X-ray analysis indicated that the initial reaction was to cupric and chromic oxides

$$2CuCrO_4 \rightarrow 2CuO + Cr_2O_3 + 3/2\ O_2 \quad , \qquad (3)$$

which was then followed by formation of cupric chromite

$$CuO + Cr_2O_3 \rightarrow CuCr_2O_4 \quad . \qquad (4)$$

Addition of 40% cupric chromite accelerated the decomposition of cupric chromate and autocatalysis was not observed. The chromite was considered to promote the direct formation of chromite from chromate without the intermediate production of chromic oxide:

$$2CuCrO_4 \rightarrow CuCr_2O_4 + CuO + 3/2\ O_2 \quad . \qquad (5)$$

X-ray and ESR analysis of CuO-Cr_2O_3 mixtures[13] have recently been interpreted to confirm the various reactions (1)-(5).

The decomposition of basic cupric chromate has also been studied[14,15] by TGA. The decomposition was found to occur in stages - the first at 450-510°C corresponding to reaction (5), the second at above 850°C corresponding to reaction (1) and finally at about 1100°C the conversion of cupric oxide to cuprous oxide:

$$2CuO \rightarrow Cu_2O + \tfrac{1}{2}O_2 \quad . \qquad (6)$$

The present work has confirmed that the processes involved in the thermal decomposition of chromate and chromite samples are those of reactions (5), (1) and (6) which correspond to stages (ii), (iii) and (iv) observed in the TGA experiments described above.

It is further evident from the relative weight losses at the various stages in the TGA that both the Propellent and Hopkins and Williams copper chromates are similar and that both contain cupric chromate and cupric hydroxide. On the other hand, the two samples of copper chromite show appreciably different behaviour in the TGA experiments. Harshaw chromite clearly has a large content of cupric oxide and relatively little cupric chromite, whereas RIC chromite appears to have no cupric oxide after the cupric chromite to cuprous chromite transition (reaction (1)) has occurred. The RIC chromite thus contains one mole or less cupric oxide per mole of cupric chromite. These conclusions are in good agreement with the analytical results for copper and chromium content.

4.2 Reaction with gaseous fuels and oxidizers

The use of metal oxides as catalysts for the oxidation of hydrocarbons has long been known[16-19]. However, the precise mechanism is still not established since catalyst studies are frequently more concerned with the relative efficacies of different catalysts than with the mechanism by which the catalyst is effective[18]. The mechanism is usually considered to involve adsorption of reactants on the surface of the catalyst followed by reaction and desorption from the surface. Support for this comes from the similarity in the patterns of catalytic activity for a range of metal oxides both for hydrocarbon oxidation and for oxygen atom recombination. However, there is some agreement that in metal oxide catalysed oxidations the metal ions in the lattice undergo redox cycles in which the hydrocarbon reacts with the metal ions in their high valency state and the ions are then reoxidized by molecular oxygen.

The effect of gaseous fuels and oxidizers on copper chromate or chromite has been reported infrequently. An early study[10] of a cupric oxide-cupric chromite catalyst stated that after use in a liquid phase hydrogenation below 300°C the cupric chromite was largely reduced to cuprous chromite by reaction (1) which competed with the reduction of cupric oxide to cuprous oxide (reaction (6)) and to metallic copper. The presence of metallic copper in the reduced catalyst was confirmed by X-ray analysis. It was found that the copper was rapidly reoxidized to cupric oxide but that the cuprous chromite required a more extended exposure (4-6 hours) to oxygen at 650°C to reoxidize it to cupric chromite. A recent paper[20] ascribes the reactivity of such cupric oxide - cupric chromite catalysts to the reduction of cupric oxide to cuprous oxide and copper but it does not elaborate on the effect of the chromite.

The present work shows that alternate exposure of catalyst to fuel and oxygen results in reproducible weight losses and weight gains respectively. The weight losses are independent of whether the fuel is ammonia, isobutene or ethylene. This suggests that the fuels react with the oxygen contained in the catalyst which is simultaneously reduced. The fact that the percentage weight changes are independent of the weight of the sample of catalyst suggest that this reaction involves the oxygen contained in the bulk of the catalyst and not just that present in the surface layer. Gas chromatographic analysis of the product gases when isobutene is passed over copper chromate showed that carbon dioxide was a product. The heat release in the reaction of fuel with oxygen in the catalyst will depend on the nature of the fuel.

On the other hand the effect of oxygen will be to reoxidize the catalyst from its reduced state. The heat release for this reaction should be independent of the nature of the fuel previously introduced.

The weight changes observed experimentally at 400-410°C may be compared with the calculated weight losses corresponding to the formation of cuprous chromite and copper as the components of the reduced catalyst. Both experimental and calculated percentage weight losses are given in Table 4. It is evident that the total weight loss on exposure to a gaseous fuel does indeed correspond to reduction of the catalyst to cuprous chromite and copper. The weight loss on heating is somewhat larger than that expected for loss of water from the cupric hydroxide. Two possible explanations are that (i) the presence of 1 or 2% of water adsorbed on the catalyst sample would increase the weight loss of the first stage with only a small effect on the other stages and (ii) the flattening of the TGA curve for the chromate between the loss of water and the onset of the chromate decomposition is not extensive and it is likely that some decomposition may already have occurred.

The possibility of adsorbed water could well explain the apparent discrepancy in the figures for the samples of RIC chromite. If the decomposition of the cupric chromite was intermediate between the two cases computed - with weight changes respectively for the third, fourth and fifth stages of 4, 1 and 1% - and there was about 4% of water present, then the percentage weight losses would be in good agreement with the experimental observations.

It is further evident that in the subsequent exposure to oxygen and fuel the redox cycle involved is that of copper - cupric oxide. Samples of Analar cupric oxide were subjected to a similar cycle of events. The total weight loss on heating with fuel was 20.5 in good agreement to the calculated loss of 20.1 for reduction to copper. Subsequent weight changes on exposure to fuel or oxygen were about 7-10% but the reproducibility was worse than for the copper chromate or chromite samples. As the cupric oxide sample after exposure to fuel and oxygen alternately was observed to have conglomerated, it is possible that this is the reason for the decreased weight changes. It also suggests that the role of the chromate/chromite may in part be related to preventing such conglomeration.

The effect of perchloric acid vapour is to give an increased weight change over that from oxygen but the interpretation of the experimental weight changes is complicated by the acid affecting only the surface layer. Visual observation of the chromate/chromite samples after exposure showed that the colour changed from black to a brownish-red. This was particularly evident with the RIC chromite, which contains the least cupric oxide. Exposure to fuel vapour after the perchloric acid resulted in a reduced overall weight loss as compared to the weight loss observed on the exposure of fresh samples of catalyst to fuel vapour. This showed that the perchloric acid had reacted with the catalyst samples irreversibly as well as by forming the chromate. After this irreversible weight increase from first exposure to perchloric acid vapour no subsequent irreversible weight gains were observed. The most pronounced effect was found with cupric oxide with a weight increase of about 21% and the reduction of the weight changes on exposure to fuel and oxidizer to about 1%. The weight increases for the other catalysts were less pronounced but were largest with the Harshaw chromite. These observations suggest that the perchloric acid reacts with the cupric oxide forming an unreactive species such as a chloride or oxychloride. The formation of oxychloride and chloride by reaction of cupric oxide with perchloric acid was confirmed by testing acid and aqueous extracts with silver nitrate solution. Oxychloride was present in appreciably greater quantity than chloride.

These observations are in general accord with the observations made by Wise et al[23] that copper chromite (Harshaw) changes colour on decomposing ammonium perchlorate showing chromate formation and that this colour change is not observed in the presence of ammonia.

4.3 Composite propellent catalysis

The role of chromate or chromite catalysts in the combustion of composite propellents may now be considered. The present work has shown that these catalysts are effective, at temperatures close to those prevailing on the propellent surface[21], in promoting the reaction of ammonia or olefins with perchloric acid or oxygen. Under the same experimental conditions, a paraffin hydrocarbon, methane, was unaffected. It has also been shown that pronounced heat release is observed both when these catalysts are exposed to fuel vapour and subsequently to perchloric acid or oxygen. Further, under the heterogeneous conditions prevailing on the surface of composite propellents, it is possible that the catalyst particles are participating in a redox cycle similar to that shown in these studies. It is therefore envisaged that the heat release on the catalyst particles on the surface of the propellent will a priori enhance the burning rate as a consequence of the increased heat transfer into the solid propellent.

Such surface reaction, which results in the reaction of a part of the fuel and the oxidizer, may also enhance the burning rate through a second effect in which the gas phase burning velocity is increased[22].

The catalyst may also be effective in other ways such as by promoting the reaction of perchloric acid vapour with solid fuel[4] or by modifying the pyrolysis mechanism of the solid fuel.

Copper chromate (propellent grade) and copper chromite (Harshaw) may be compared by the amount of oxygen available for initial reaction with the fuel. This is greater (17.0%) for chromate than for chromite (14.2%) but this is offset to some extent by the water present in the chromate (8.9%). On the other hand the amount of oxygen involved in the subsequent redox cycle (CuO - Cu_2O - Cu) is greater with chromite (12.2%) than with chromate (8.0%). Their relative merits as burning rate or ignition catalysts will depend on which factor is the most significant for the practical conditions concerned. It should be emphasised that after the initial reduction the chemical species present from both copper chromate and copper chromite are the same, and the samples then differ only in the relative amounts of copper oxide and chromite.

5 CONCLUSIONS

The thermal decompositions of copper chromate and chromite have been shown by TGA-DTA studies to proceed by the successive stages: cupric chromate → cupric chromite → cuprous chromite followed by (if cupric oxide is present) cupric oxide → cuprous oxide as the temperature is increased from ambient to about 1100°C.

Alternate successive exposure of the catalyst at a temperature close to that on the surface of a burning propellent to fuel (ammonia, isobutene or ethylene) and oxygen has shown that after initial reduction to cuprous chromite and copper, a redox cycle occurs between cupric oxide - cuprous oxide - copper which is associated with exothermic reactions both in the reduction and oxidation stages of the cycle. Methane was ineffective and did not participate in a redox cycle. When perchloric acid was used as oxidizer, an irreversible weight change occurred, along with the oxidation part of the redox cycle.

It is concluded that the enhanced heat release from such reactions on catalyst particles on the surface of the propellent is one route by which the burning rate is enhanced.

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Table 1

NOMINAL FORMULAE AND SOURCES OF THE CATALYST SAMPLES

Catalyst	Source nominal formula
Copper chromate	Propellent grade $CuCrO_4.2Cu(OH)_2$ Cu as CuO 62; Cr as CrO_3 28
Copper chromate	Hopkins and Williams Ltd. $CuCrO_4.2Cu(OH)_2$
Copper chromite	Harshaw Chemical Co. Harshaw Catalyst Cu 0202p Cu as CuO 82; Cr as Cr_2O_3 17
Copper chromite	Research Inorg. Chem. Co. 99%
Cupric oxide	Hopkins and Williams Ltd. CuO 'Analar' grade

Table 2

COPPER AND CHROMIUM CONTENTS AND EMPIRICAL FORMULAE OF THE CATALYST SAMPLES

Catalyst	Copper as Cu	Chromium as Cr	Empirical formula
Propellent chromate	48.4	13.7	$CuCrO_4$. 1.75 $Cu(OH)_2$
H. & W. chromate	46.0	14.4	$CuCrO_4$. 1.4 $Cu(OH)_2$
Harshaw chromate	63.5	12.1	$CuCr_2O_4$. 7.0 CuO
RIC chromite	33.6	29.9	$CuCr_2O_4$. 0.9 CuO
Cupric oxide	78.5	-	98.2% CuO

Table 3

POSITION OF ENDOTHERMS AND EXOTHERMS IN THE DIFFERENTIAL THERMAL ANALYSIS OF THE CATALYST SAMPLES

Sample	Endotherms	Exotherms
Propellent chromate	356, 479, 780, 956	497
H. & W. chromate	357, 471, 769, 935	398
Harshaw chromite	742*, 984	-
RIC chromite	120*, 346*, 798	-
Cupric oxide	971	-

* These endotherms were small, although definite.
Endotherm and exotherm temperatures in °C.

Table 4

EXPERIMENTAL AND CALCULATED WEIGHT CHANGES FOR COPPER CHROMATE AND CHROMITE SAMPLES

Catalyst	Experimental percentage weight changes			Empirical formula	Calculated percentage weight changes					
	Heat	Heat and fuel	Subsequent oxygen/fuel		Loss of H_2O	$CuCrO_4 \downarrow CuCr_2O_4$	$CuCr_2O_4 \downarrow Cu_2Cr_2O_4$	$CuO \downarrow Cu_2O$	$Cu_2O \downarrow Cu$	Total
Propellent chromate	11.0	27.3	8.0	$CuCrO_4 \cdot 1.75Cu(OH)_2$	9.0	6.8	2.3	4.0	4.0	26.1
H. and W. chromate	10.0	25.0	6.8	$CuCrO_4 \cdot 1.4\ Cu(OH)_2$	8.0	7.5	2.5	3.5	3.5	25.0
Harshaw chromite	0.5	14.0	12.0	$CuCr_2O_4 \cdot 7.0CuO$	-	-	2.0	6.1	6.1	14.2
RIC chromite	3.7	10.0	2.0	$CuCr_2O_4 \cdot 0.9CuO$	-	-	(5.1 (2.6*	0 2.6	0 2.6	5.1 7.8*

*Calculated assuming $CuCr_2O_4 \rightarrow \frac{1}{2}Cu_2Cr_2O_4 + \frac{1}{2}Cr_2O_3 + \frac{1}{2}O$

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20	H. Ohtsuka K. Aomura N. Tomita K. Hashimoto O. Takada	Copper oxide and Adkins' copper oxide-copper chromite catalysts. Hokkaido Daigaku Kogakubu Iho 1966, No.41, 199-230; Chem. Abstr., 69 (1968), 702172
21	J. Powling	Experiments relating to the combustion of ammonium perchlorate-based propellents. Eleventh Symposium (International) on Combustion, pp 447-456 Pittsburgh, The Combustion Institute (1967)
22	A.R. Hall G.S. Pearson	The mechanism of the catalysis of ammonium perchlorate combustion: Effect of pre-flame heat release on burning velocity of the gas phase flame. Combustion and Flame, submitted
23	W.A. Rosser S.H. Inami H. Wise	Thermal decomposition of ammonium perchlorate. Combustion and Flame 12 (1968), 427-435

<u>ATTACHED</u>:-

Drgs. RP 4810-4813
Detachable abstract cards

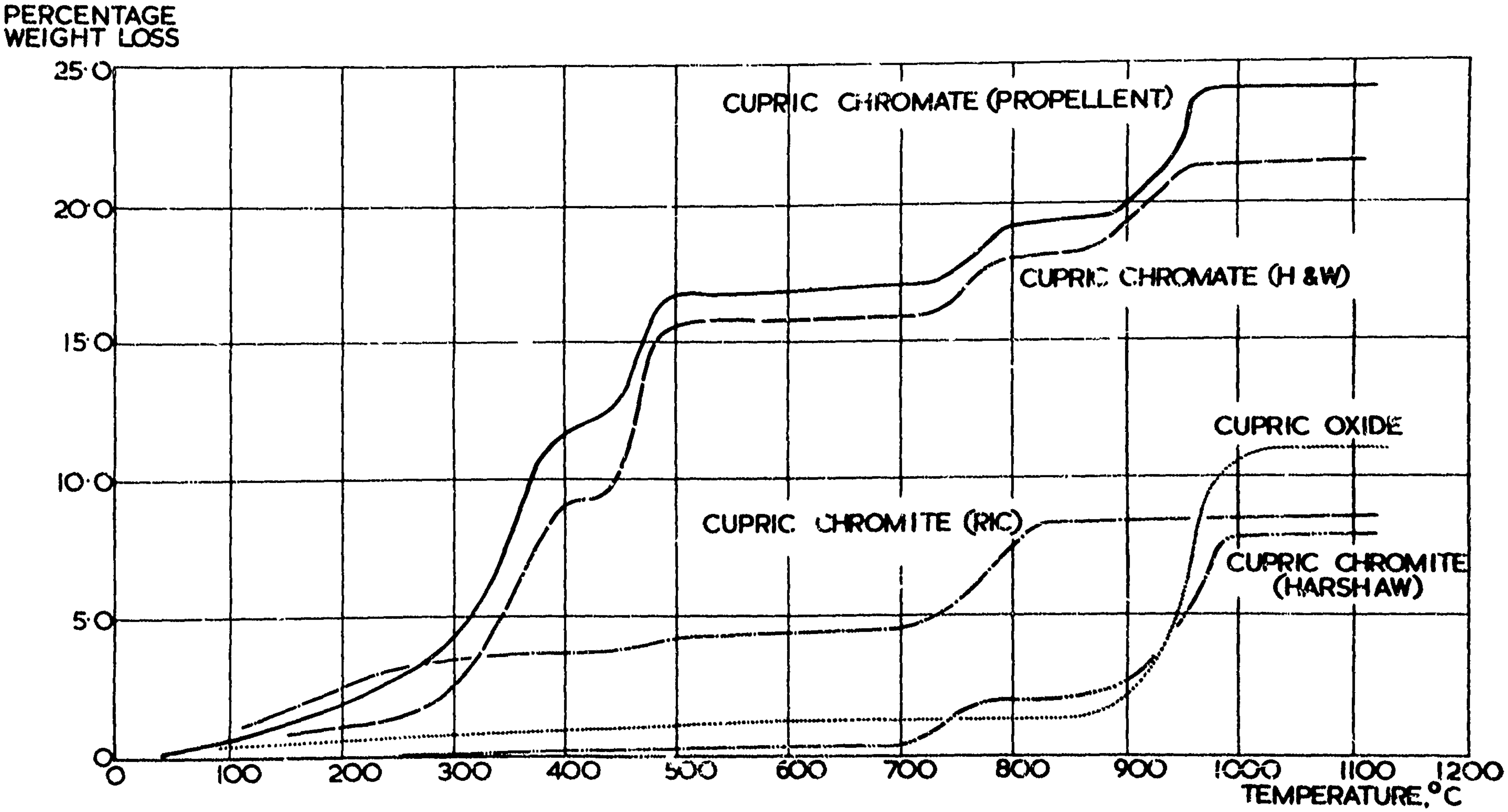

FIG. 1 THERMOGRAVIMETRIC RESULTS FROM HEATING OF THE CATALYST SAMPLES AT 5 DEG. C MIN^{-1} IN NITROGEN

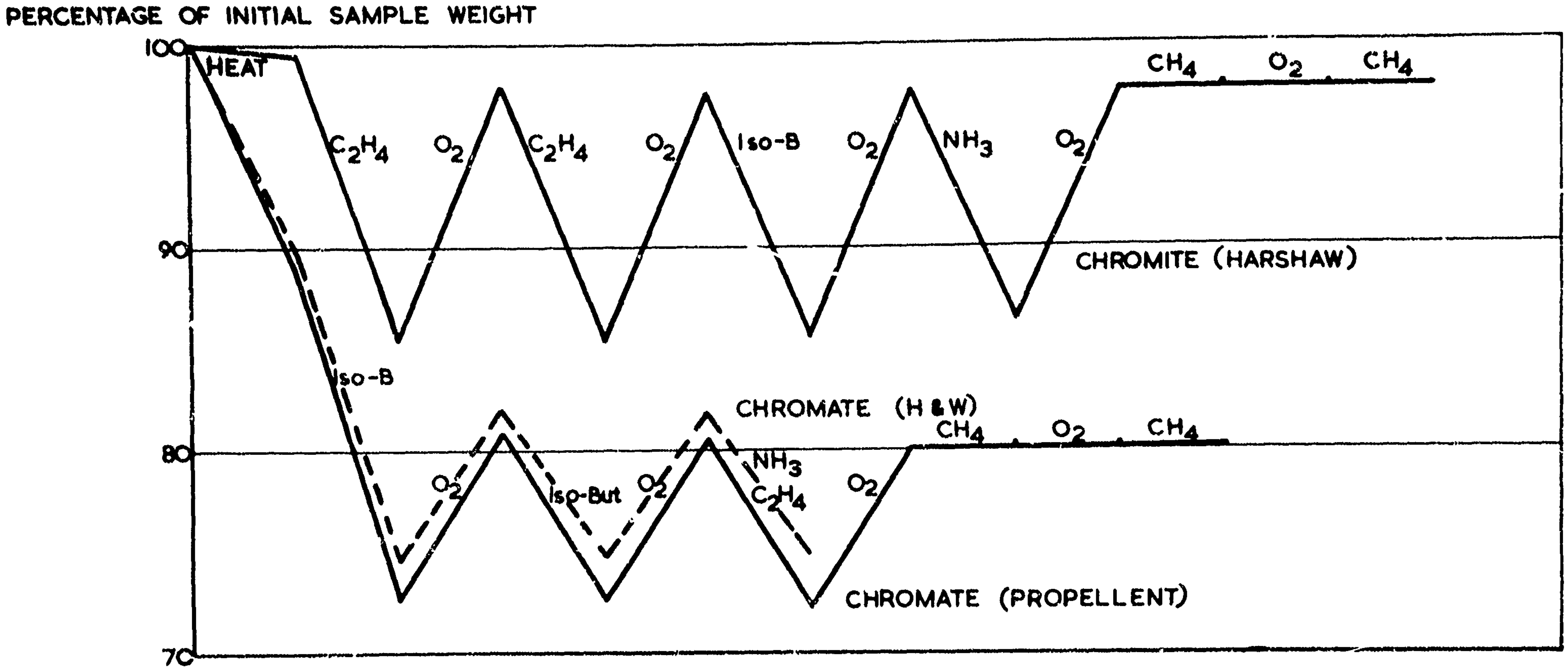

FIG.2 PERCENTAGE WEIGHT CHANGES OBSERVED ON ALTERNATE EXPOSURE OF CATALYST SAMPLES TO FUEL (AMMONIA, ISOBUTENE, ETHYLENE OR METHANE) AND OXYGEN

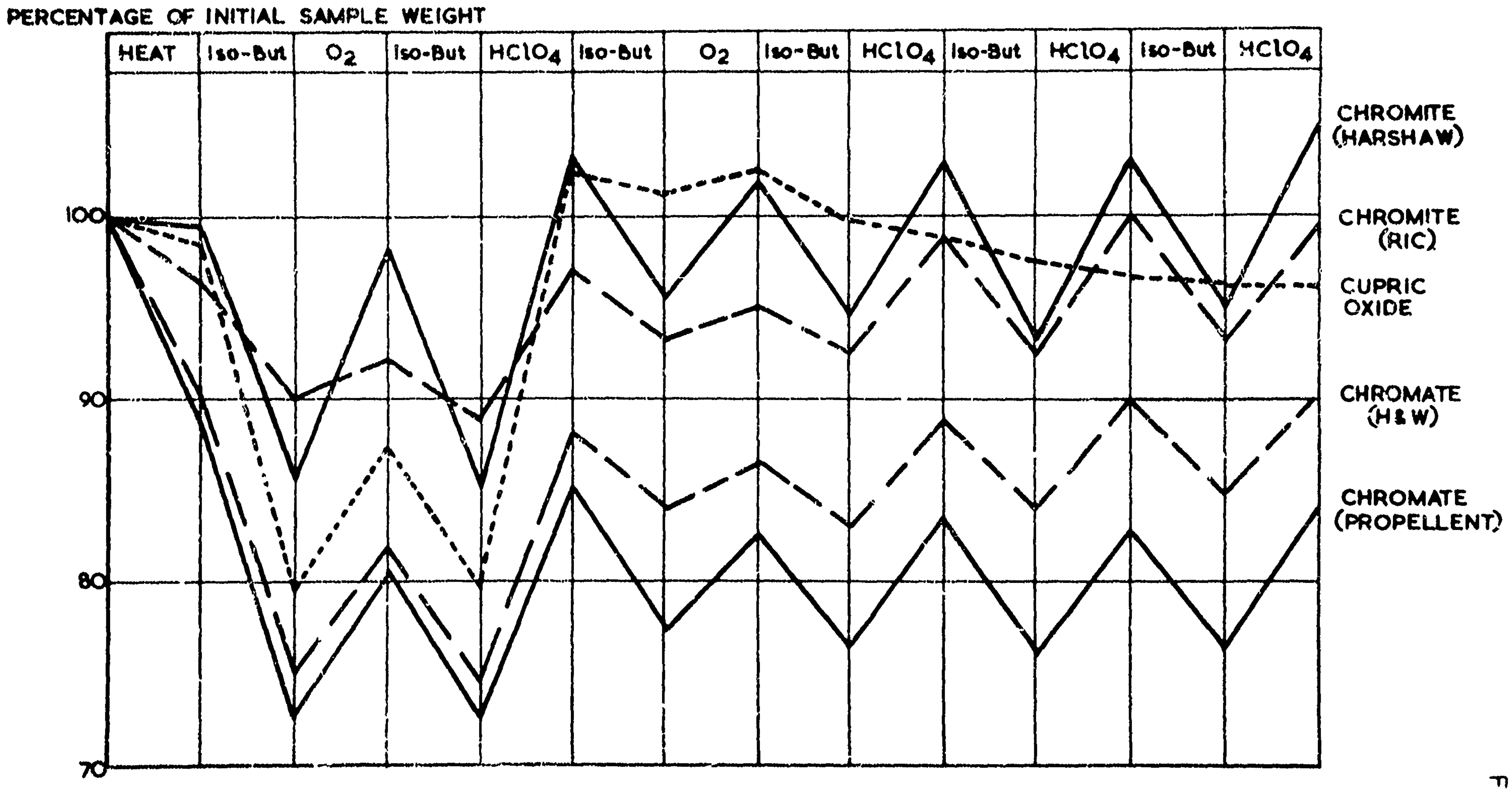

FIG. 3 PERCENTAGE WEIGHT CHANGES OBSERVED ON ALTERNATE EXPOSURE OF CATALYST SAMPLES TO ISOBUTENE AND OXIDIZER (PERCHLORIC ACID OR OXYGEN)

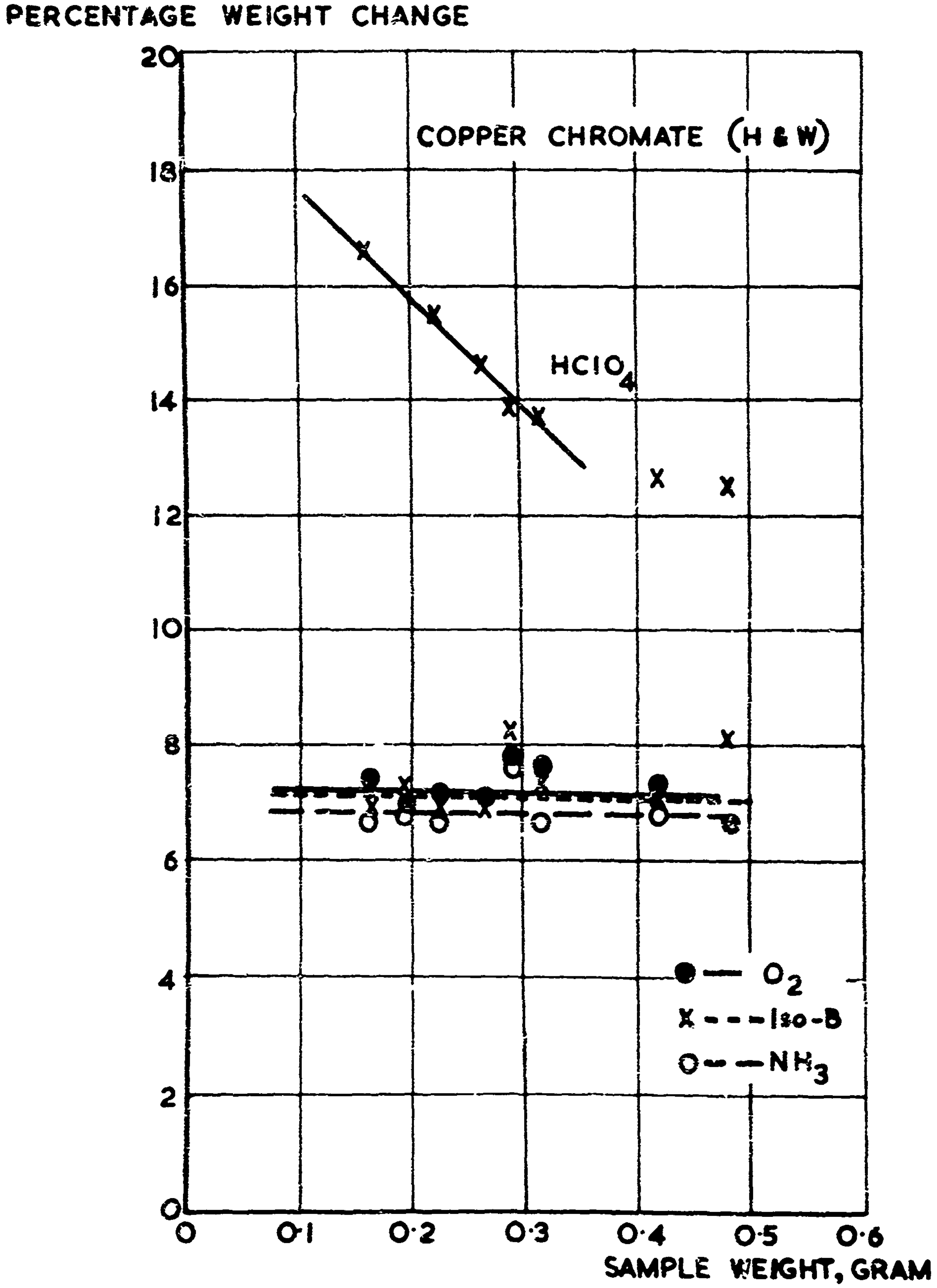

FIG.4. PERCENTAGE WEIGHT CHANGES WITH VARIOUS REACTIVE GASES FOR DIFFERENT WEIGHTS OF COPPER CHROMATE (H & W)

DETACHABLE ABSTRACT

Pearson, G.S.

621.455-846 :
546.128 :
546.56 :
546.76

COMPOSITE PROPELLENT CATALYSTS : COPPER CHROMATE AND COPPER CHROMITE

Rocket Propulsion Establishment Technical Report 69/7 May 1969

The thermal decompositions of copper chromate and copper chromite have been examined by simultaneous thermogravimetric analysis and differential thermal analysis. Decomposition proceeds in successive stages ultimately yielding cuprous chromite and cuprous oxide from both copper chromate and copper chromite.

Alternate successive exposure of the catalyst at 400-420°C to fuel (ammonia, isobutene or ethylene) and oxygen showed that after the initial reduction, a redox cycle occurred between cupric oxide and copper. Both stages of the redox cycle were associated with exothermic reactions. No

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The relevance of these results to the mechanism of composite propellent catalysis is discussed.

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