Thermochimica Acta, 79 (1984) 205–216
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE THERMAL DECOMPOSITION OF COPPER/CHROMIUM CARBONATE

ASIF S. BHATTI and DAVID DOLLIMORE

Department of Chemistry, The University of Toledo, Toledo, OH (U.S.A)

NEIL BLACKMORE

University of Salford, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)

(Received 30 March 1984)

ABSTRACT

This study details the preparation of copper/chromium carbonate mixtures using the coprecipitation method to obtain much finer mixtures than could possibly be achieved by grinding. Samples were prepared in the following ratios of copper carbonate/chromium carbonate: 1 : 3, 1 : 2, 1 : 1, 2 : 1, 3 : 1. Heat treated residues of these coprecipitates were then used as the basic catalyst material in the "rocket fuel", prepared by mixing ammonium perchlorate and styrene monomer, and polymerising at 50 °C using benzoyl peroxide. DTA were run on ammonium perchlorate and the prepared polystyrene for identification purposes. Samples of ammonium/catalyst "rocket fuel" were run on the DTA unit to determine catalyst efficiency.

INTRODUCTION

Modification of the burning rate of composite propellants based on ammonium perchlorate in a matrix of polymeric fuel is frequently achieved by the addition of small amounts of various substances, one of which is copper chromite [1].

Copper chromite is normally prepared by grinding together copper carbonate and chromium carbonate and heat treating at ~ 800 °C for ~ 2 h. This is considered to be a fairly inefficient method of preparation as complete mixing is unlikely and the resultant heat treated residue is likely to contain large quantities of copper and chromium oxides.

To replace this method a coprecipitation of copper and chromium carbonates was carried out, the object being to obtain a much finer mixture than could possibly be achieved by grinding. Heat treated residues of these coprecipitations were then used as the basic catalyst material.

0040-6031/84/$03.00

EXPERIMENTAL

Materials

Samples of mixed copper/chromium carbonates were prepared by coprecipitation from copper and chromium nitrate mixtures with sodium carbonate in excess. The precipitates were prepared in ~ 80 g quantities (dry wt.). They were all prepared at room temperature, allowed to settle, and the mother liquor poured off, more water was poured in and mixed with the sludge and the process repeated several times. Finally, they were filtered, washed thoroughly with distilled water, and dried overnight at 100–110 °C.

Samples were prepared in the following ratios of copper carbonate/chromium carbonate: 1 : 3, 1 : 2, 1 : 1, 2 : 1, 3 : 1. As the maximum catalyst efficiency was expected to be around 1 : 2 copper carbonate/chromium carbonate, investigations were limited to 1 : 1, 1 : 2 and 1 : 3 copper/chromium. These were then heat treated at 700, 800 and 900 °C for different periods of time, the emphasis being on 800 °C. Ammonium perchlorate (AP) samples where used were prepared by powdering crystalline technical grade reagent.

The ammonium perchlorate catalyst mixtures were prepared by mixing powdered AP with powdered catalyst until a constant grey colour was obtained. These ratios of catalyst/AP were varied from 0.5–5%.

Polystyrene was prepared from the polymerisation of styrene with benzoyl peroxide at 50 °C.

The "rocket fuel" itself was prepared by mixing the AP/catalyst mixture with benzoyl peroxide and styrene monomer and polymerising at 50 °C.

An alternative method of preparation by dissolving polystyrene in toluene, adding AP and catalyst and then drying, was also tried but this left a sticky residue.

Thermal analysis

Rising temperature TG

The Stanton-Redcroft thermobalance was used as previously described [6]. The 1 : 1, 1 : 2 and 1 : 3 copper carbonate/chromium carbonate samples were used in an attempt to obtain some idea of the mechanism of copper chromite formation. Also, a sample of rocket fuel was used to enable kinetic studies to be made.

Differential thermal analysis

The DuPont 900 apparatus was used with a 1000 °C cell. The temperature of the system is recorded near the sample crucible, and as this is subjected to an extremely large exotherm in the case of AP/catalyst mixtures the trace for the temperature of the system shows a negative slope during the decrease of the exothermic peak, caused by the system cooling to meet its temperature programming rate. To obtain more acceptable peaks the sample and reference crucibles were reversed. It should be stressed that the temperature of peaks in this system, if there is a rapid violent exotherm only, represents the temperature immediately before ignition.

DTAs were run on ammonium perchlorate (powdered) and prepared polystyrene for identification purposes. Samples of AP/catalyst and "rocket fuel" were run on the DTA to determine catalyst efficiency.

Surface area measurements

Surface areas were quantified by the single point method.

RESULTS

Rising temperature TG

The results of the decomposition of 1 : 1, 1 : 2 and 1 : 3 copper/chromium carbonates were obtained as weight loss vs. temperature plots. The lower temperature plots shown in Fig. 1 are basically a mixture of the decomposition characteristics of copper carbonate and chromium carbonates the 1 : 3 being very similar to the decomposition of pure chromium carbonates. At

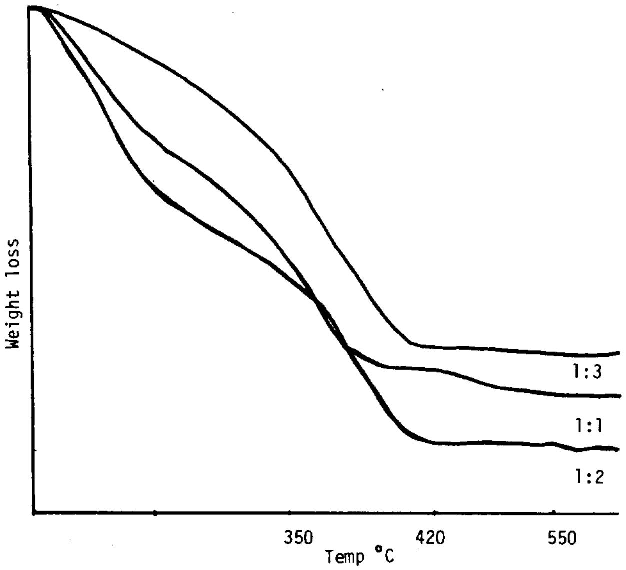

Fig. 1. Plot of weight loss vs. temperature for the lower part of the decomposition of various mixtures of copper/chromium carbonates.

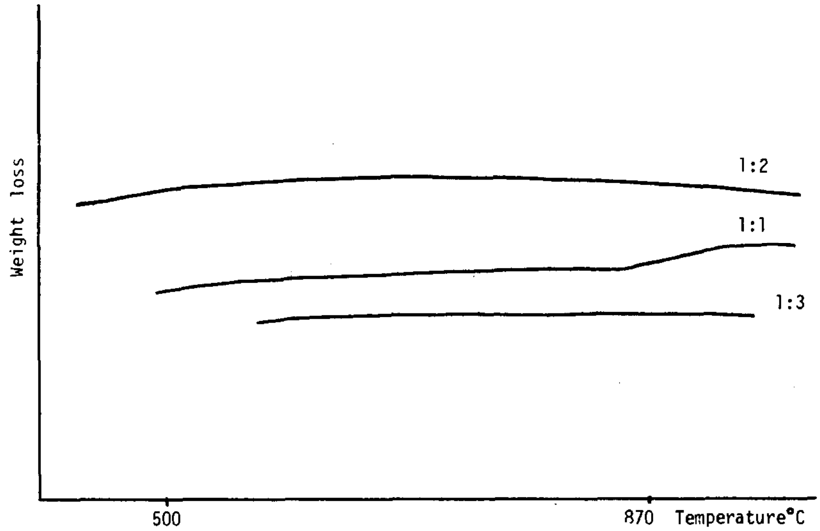

Fig. 2. Plot of weight loss vs. temperature for the upper part of the decomposition of various mixtures of copper/chromium carbonates.

the end of this decomposition a mixture of copper and chromium oxides should be present after about 550 °C. The higher end "decompositions" are shown in Fig. 2. Above these temperatures it is expected that copper chromite is present in varying proportions. However, only the 1 : 1 showed any appreciable weight loss, commencing at 869 °C. Of the other two samples the 1 : 3 showed no real weight change and the 1 : 2 showed an apparent increase in weight.

Differential thermal analysis

The results of the DTA on the ammonium perchlorate, polystyrene and catalyst, and mixtures thereof are shown in Figs.`4 and 6 and summarized in Table 1, which shows the temperature of exotherms and the number of exotherms vs. the sample size and heating rate.

Surface area measurement

The surface area measurement of the heat treated copper and chromium carbonate mixtures was carried out using the single point method and calibration described by Haynes [3] and Klyacho-Gurvick [4]. The results of the surface area measurements vs. time of heating and temperature of the various mixed carbonate compositions are shown in Table 2.

TABLE 1

Data on exothermic peaks of AP, catalyst and polystyrene

Sample description	Weight (mg)	Position of temperature measuring thermocouple	Heating rate (°C $\min^{-1}$)	No. of peaks	Temp. of peaks (°C)
Ammonium perchlorate powder	Large	Reference crucible	10	2	303,366
Ammonium perchlorate powder	Small	Reference crucible	20	2	303,377
Ammonium perchlorate powder	Large	Sample crucicle	20	1	329
AP/catalyst (1%)	Medium	Sample crucible	20	1	344
AP/polystyrene/catalyst (1%)	Medium	Sample crucible	20	1	334
AP/polystyrene	Medium	Sample crucible	25	1	344
AP/catalyst (1%)	Small	Reference crucible	10	2	301, 351
AP/catalyst (1%)	43	Reference crucible	10	1	299
AP/catalyst (1%)	Small	Reference crucible	10	2	301, 351
AP/catalyst (5%)	39	Reference crucible	10	2	304, 341
AP/catalyst (5%) finer ground	10.2	Reference crucible	10	2	295, 341
AP/catalyst (5%) finer ground	36.4	Reference crucible	10	1	307
AP/polystyrene/catalyst (1%)	25.8	Reference crucible	10	1	301

TABLE 2

Surface area of heat treated copper and chromium carbonate mixtures

Ratio basic copper carbonate to chromium	Temperature (°C)	Time of heating (h)	Surface area ($m^2 g^{-1}$)
1:1	800	1	0.747
1:2	800	1	0.685
1:3	800	1	1.130
1:1	800	2	1.618
1:2	800	2	0.693
1:3	800	2	
1:1	800	5	4.2182
1:2	800	5	1.248
1:3	800	5	2.311
1:1	800	24	0.812
1:2	800	24	1.4941
1:3	800	24	2.514
1:1	700	2	3.609
1:2	700	2	1.764
1:3	700	2	1.529
1:1	900	2	3.351
1:2	900	2	2.753

TABLE 3

Weight losses due to heat treatment of various copper and chromium carbonate mixtures, and estimated percentages of copper chromite in residue

Copper carbonate/ chromium carbonate ratio	Temp. (°C)	Time of heating (h)	% Wt. after heating	% Wt. after dissolving residue in HCl
1:1	800	1	60.51	60.09
1:1	800	2	59.75	
1:1	800	24	59.51	
1:2	800	1	57.26	49.94
1:2	800	2	57.26	
1:2	800	24	56.99	58.37
1:3	800	1	66.95	56.26
1:3	800	2	67.00	53.18
1:3	800	24	66.56	
1:1	800	5	59.35	65.99
1:2	800	5	53.56	50.13
1:3	800	5	66.26	52.87
1:1	900	2	59.46	
1:2	900	2	54.33	
1:3	900	2	65.79	55.73
1:1	700	2	61.11	
1:2	700	2	57.22	
1:3	700	2	66.50	56.93

Chemical analysis

Copper chromite contents of the heat treated mixed carbonates (i.e., residue undissolved in concentrated hydrochloric acid) are summarized in Table 3 along with the weight loss due to heating of the mixed carbonate.

DISCUSSION

Rising temperature TG

The TG data indicate that 1 : 1 copper/chromium carbonate gave the most chromite on the supposition that the higher temperature weight loss (Fig. 2) can be attributed to the formation of copper chromite. This was confirmed by chemical analysis (Table 3).

Chemical analysis

The chemical analysis carried out on the heat treated carbonates by gravimetric quantification of the insoluble residue after dissolution in concentrated hydrochloric acid (Table 3) revealed that 1 : 1 copper/chromium carbonate heat treated samples gave the highest quantity of copper chromite. All the 1 : 3 samples from heat treatment were evaluated by this method. In the 700–900 °C range very little difference was noticed in the percentage weight of the residue due to temperature or time of heating. Thus, only a few of the 1 : 1 and 1 : 2 samples were investigated as these were expected to act similarly and in order to preserve the catalyst samples. From the investigation the 1 : 1 sample had the highest copper chromite content (60–65%) of the heat treated residues.

Differential thermal analysis

DTA was first used to examine the "raw materials" in the production of "rocket fuel", namely ammonium perchlorate and polystyrene.

DTA can be used to aid the identification of the polymer through the comparison of the curves of the unknown with standard reference materials, i.e., as a fingerprint technique [5]. Figure 3 shows a typical DTA curve for a polymeric material in an air atmosphere. The peaks are: (A) crystallization; (B) melting; (C) oxidation. From the DTA on the polystyrene prepared by the polymerization of styrene monomer with benzoyl peroxide initiator (Fig. 3), it is evident that the "polystyrene" prepared is in fact a polymeric material (which is not unexpected).

It has been reported [2] that ammonium perchlorate is stable at room temperature but decomposes at a measurable rate on heating, 30% decom-

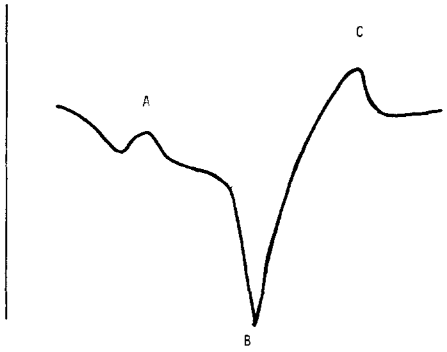

Fig. 3. DTA for prepared polystyrene in air.

posing at $T < 325\,^{\circ}C$ this decomposition being autocatalytic and the completion of the decomposition occurs at $T > 375\,^{\circ}C$.

In this study, with a sample heated at 10 °C min^{-1}, two peaks were obtained on the DTA at 303 and 366 °C. Allowing for different reaction vessels, atmospheres, and heating rates, this indicates that the sample was, in fact, ammonium perchlorate.

The study of rocket fuels began by the preparation of ammonium perchlorate–polystyrene–catalyst mixtures. These were prepared as described earlier by crushing the AP and catalyst and mixing with benzoyl peroxide and styrene monomer. The resultant mixture was then left in an oven. The preparation of a sample of rocket fuel with a predetermined concentration of polystyrene proved to be a problem as much of the styrene monomer evaporated in the oven before polymerization. Work was, therefore, largely limited to thermal analysis of only those AP/catalyst mixtures which could be reproducibly prepared with respect to the ratio of ingredients. The catalyst used throughout this study was the heat treated residue obtained by heating 1 : 1 mixtures at 800 °C for 2 h. The 1 : 1 mixture was chosen in preference to the 1 : 2 or the 1 : 3 mixture as it contained greater amounts of copper chromite. Furthermore, it appeared more homogeneous than the 1 : 3 samples which were greenish black and it was crushed more easily than either the 1 : 2 or 1 : 3 samples, which was a useful property for the preparation of a finely divided mixture. As more of the 1 : 1/800 °C/2 h sample was available than any other 1 : 1 sample, this was used as catalyst. This temperature was also used in previous work on catalysts prepared by grinding together copper and chromium carbonates, and the resultant mixture was heat treated at 800 °C for 2 h to obtain the catalyst.

Initially, samples of AP, AP/catalyst and AP/polystyrene/catalyst were investigated by DTA under nitrogen at a flow rate of 0.2 l min^{-1} and a heating rate of 20 °C min^{-1}. No attempt was made to measure the amount of sample tested and the temperature-measuring thermocouple was in the sample crucible. This resulted in the oddly shaped exotherms shown in Fig.

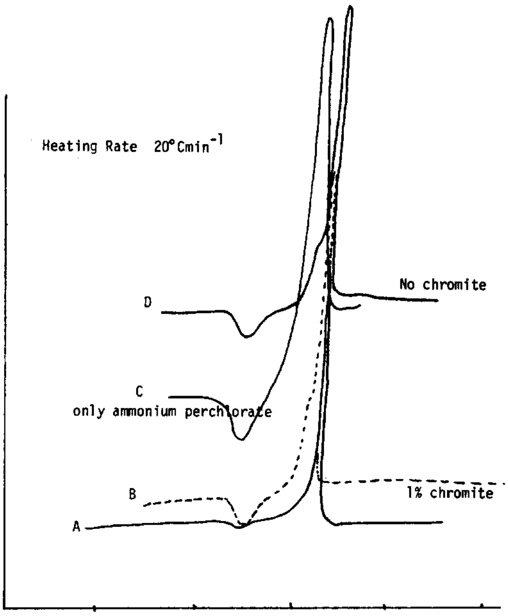

Fig. 4. DTA on mixes of ammonium perchlorate, polystyrene and chromite.

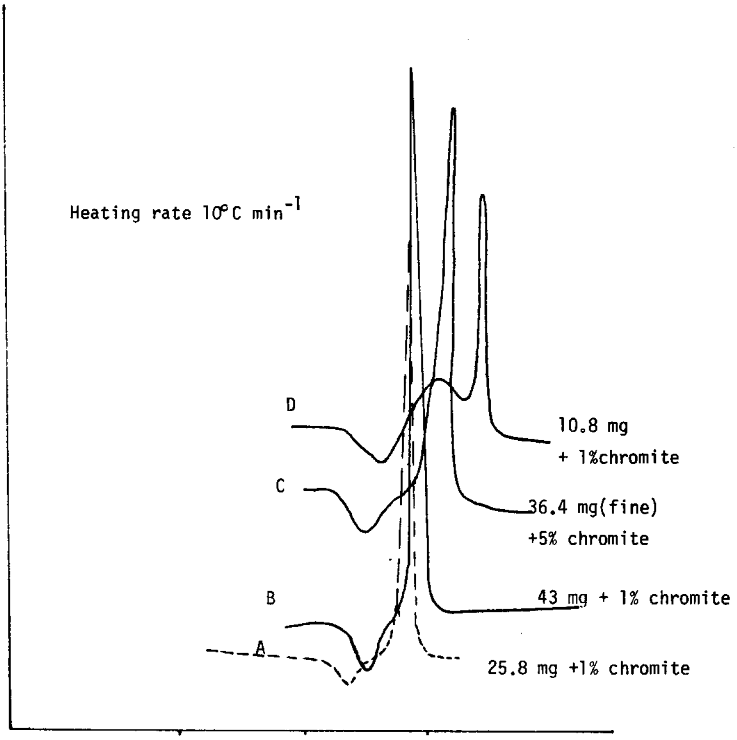

Fig. 5. DTA on mixes of different weights.

4. It was found under these conditions that instant deflagration of all catalysed samples occurred. Some of the uncatalysed samples also exhibited instant deflagration, i.e., AP/polystyrene, Fig. 4D. This was initially attributed to residues of catalyst remaining in the sample crucible from previous experiments. To avoid this the sample crucible was boiled in concentrated nitric acid to remove any copper chromite that was difficult to wash out. However, even under these conditions AP showed only one peak instead of two (Fig. 4C). A possible explanation is that the heating rate might be high enough so that when combined with the heat of the first exotherm in the decomposition of ammonium perchlorate this was enough to set off the second exotherm, the two exotherms then appearing as one large exothermic change.

In order to counter this the heating rate was reduced to 10 °C min^{-1}, and, to obtain more conventional exotherms, the temperature thermocouple was

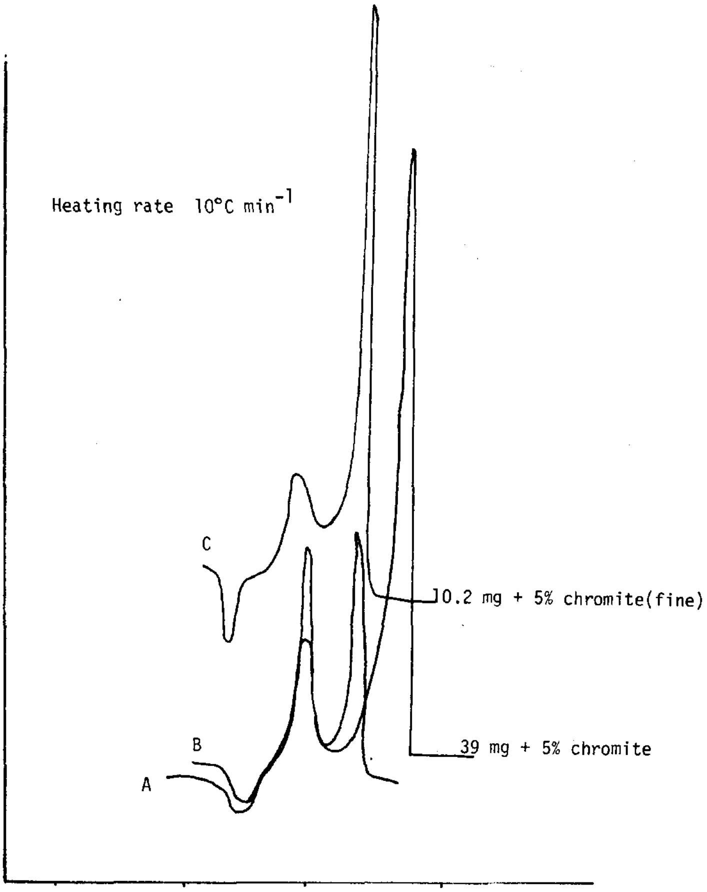

Fig. 6. DTA on mixes of different weights.

placed in the reference crucible. The resultant DTA traces are shown in Figs. 5 and 6. Under these conditions two exotherms were noted for AP (Fig. 6B). However, the catalysed samples sometimes showed one exotherm and sometimes two, even with the same AP/catalyst samples. It became apparent that the size of the sample was having an effect on this. Figure 5A shows that a large sample (25.8 mg) produced only one exotherm, whilst Fig. 5D shows that a small sample of the same AP/catalyst preparation (10.8 mg) showed two exotherms. This could be attributed to the larger sample producing more instantaneous heat from the first exotherm and hence setting off the second. In the decomposition of the smaller sample not enough heat is generated to raise the temperature of the crucible sufficiently to set the second exotherm off. The samples were subsequently weighed. Figures 6A and 5C show DTA traces of the same catalyst preparation (5% catalyst/AP). Figure 6A shows two peaks and Fig. 5C only one peak. The only difference between the experimental conditions of the two experiments was that one sample was finer ground than the other, i.e., Fig. 5C. Thus, it was concluded that particle size had an effect on the reaction pathway.

In previous reports [7] powder samples were prepared by ball milling crystalline AP and sieving into fractions. The particle size was limited to 61–88 μm. However, in this report there was no measurement and maintenance of particle size. From the results obtained it is apparent that there is a need for constancy of particle size. Initially, catalytic efficiency was estimated by the temperature of instant deflagration, i.e., by using amounts of material that gave rise only to one peak. This was found to be scarcely changed by the amount of catalyst present.

Amounts of material that showed two peaks were then studied when differences in catalytic efficiency can be seen. Using small samples the change in temperature of exotherms can be seen.

	1st peak (°C)	2nd peak (°C)
AP only	303	377
AP + 1% catalyst	301	351
AP + 5% catalyst	295	341

It can thus be seen that the amount of catalyst present does effect the exothermic characteristics of the decomposition of ammonium perchlorate.

To determine the burning rate of propellant Rastogi et al. [8], mixed AP with viscous prepolymer and put the resultant mixture into glass moulds. This was then cured for 10–12 days and the glass moulds broken. The propellant strands were held vertically and ignited electrically. The burning rate was the time required for a fixed length to burn. This seems to be an excellent method but in future studies "isothermal" DTA runs might also lead to an alternative procedure.

REFERENCES

1 G.S. Pearson, Combust. Flame, 14 (1970) 73.
2 W.A. Rosser, S.H. Inami and H. Wise, Combust. Flame, 12 (1968) 427.
3 J.H. Haynes, Clay Miner. Bull., 4 (1959) 69.
4 A.L. Klyacho-Gurvick, Izv. Akad. Nauk., SSSR, Otd. Khim. Nauk, (1961) 1884; Eng. Trans., (1961) 1756.
5 R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, London, 1972.
6 Stanton-Redcroft, Technical Information Sheet No. 102.
7 S.H. Inami, Y. Rajapakse, R. Shaw and H. Wise, Combust. Flame, 17 (1971) 189.
8 R.P. Rastogi, G. Singh and R.R. Singh, Combust. Flame, 30 (1977) 118.