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COMBUSTION INSTABILITY OF SOLID PROPELLENTS: EFFECTS ON CTPB PROPELLENT OF OXIDIZER/FUEL RATIO AND ADDITION OF FERRIC OXIDE ($Fe_2 0_3$) [R]

by

R. D. Gould

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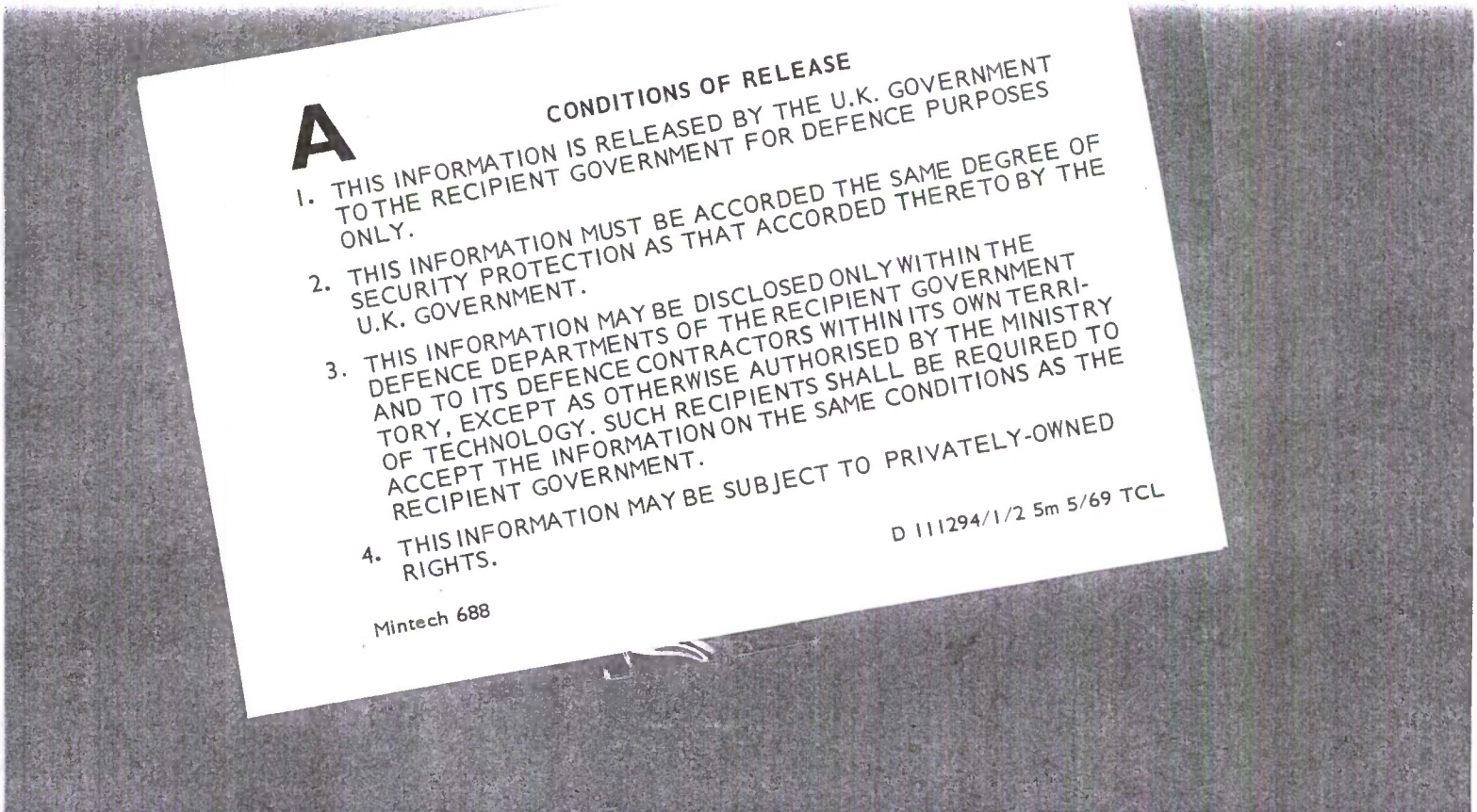
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Technical Report 69/9

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SUMMARY

The effects of compositional changes on the stability of combustion of a composite propellent based on ammonium perchlorate and carboxy-terminated polybutadiene (CTPB) have been investigated. A 50.8 mm diameter T-burner was used to study the stability in the frequency range 0.7 to 4.0 kHz at a mean pressure of 6.894 MN/m^2 (1000 psig). Ferric oxide has a small destabilizing effect on the combustion of CTPB propellents, whereas changes in the oxidizer/fuel ratio have a more complex effect. When simple propellent mixes of CTPB rubber/ammonium perchlorate and polyisobutene (PIB)/ammonium perchlorate are compared, the propellent based upon CTPB rubber as fuel appears to be relatively more stable.

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1 INTRODUCTION

Combustion instability in solid propellent rocket motors is still a perplexing problem to motor designers. A major difficulty lies in predicting the degree of instability of a new propellent in a motor environment. Double base[1,2] propellents and composite[3] propellents based upon ammonium perchlorate (AP) and polyisobutene (PIB) have been studied at the Rocket Propulsion Establishment and some conclusions have been reached about the effects of changes in the propellents on their combustion characteristics. Another composite propellent system is that utilizing ammonium perchlorate with carboxy-terminated polybutadiene (CTPB) as binder. This Report describes studies which have been carried out in the intermediate frequency range, 0.7 - 4.0 kHz, using a 50.8 mm diameter T-burner with a group of CTPB propellents. The compositional variables selected for this study were oxidizer/fuel ratio and the addition of ferric oxide to the propellent. This additive is frequently added to enhance the burning rate. The relative stabilities of the two types of composite propellent, based upon PIB and CTPB, are compared.

The results are discussed in relation to some results obtained with CTPB propellents by Brown et al.[4,5,6] of United Technology Center.

2 EXPERIMENTAL

The T-burner used for these experiments has already been described[3,7]. It consists basically of a tube, 50.8 mm internal diameter, closed at both ends in which the gas oscillates in the fundamental longitudinal mode. The burner tube length may be varied so that frequencies in the range 0.7 - 4.0 kHz can be studied. An orifice 12.7 mm diameter located centrally in the burner tube is connected to a 0.11 m^3 surge tank. The system is pressurized with nitrogen to a pressure of 6.894 MN/m^2 (1000 psig) before firing and the two propellent samples, located at each end of the burner tube, are ignited simultaneously by small cartons containing 0.4 g of a standard pyrotechnic composition, SR 371C. The pressure in the burner tube is measured by quartz piezo-electric transducers, Kistler type 601, and recorded photographically.

The CTPB propellent charges were prepared by pouring 35 g of the propellent into an end cap, vibrating to remove entrained air and finally curing at $+60^{\circ}C$ for one week. The thickness of the resulting disc of propellent was 10.2 mm (0.4 inch). The compositions and some of the ballistic properties of the propellents used for this work are given in the table.

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3 RESULTS

All the firings reported here were carried out at a mean pressure of 6.894 MN/m^2, which is representative of practical solid propellent motor operation.

The method of calculation of the acoustic response from the experimental data has already been described[7]. The acoustic responses for the four propellents used in this work are shown as a function of frequency in Fig.1.

In the majority of T-burner firings a steady maximum pressure amplitude was reached when the acoustic losses and gains for the system were balanced. This has been used as a further guide to the unstable burning characteristics of the propellent. It is shown as a function of frequency for the propellents where the oxidizer/fuel ratio was varied (Fig.2) and also where 1% of ferric oxide was added to one of the propellents (Fig.3).

4 DISCUSSION

4.1 Variation of oxidizer/fuel ratio

The table shows that as CTPB propellents become less fuel-rich the burning rate increases, thus being similar to plastic propellents.

It is evident from Fig.1 that the most fuel-rich propellent, C 50/12, has the highest acoustic response and is therefore most prone to instability. This is confirmed by Fig.2 which shows that composition C 50/12 supports the highest amplitude of pressure oscillations. The two propellents C 53/1 and C 54/1 appear similar both in their acoustic response and in the maximum pressure amplitude which they can sustain. It would seem therefore to be an advantage, both in stability and performance (table), to use the less fuel-rich propellents. However, their low temperature physical properties are less acceptable than those of C 50/12, but they are still usable at temperatures down to $-40^{\circ}C$.

4.2 Comparison of CTPB propellents with plastic propellents

The results for plastic propellents with a range of oxidizer/fuel ratios have been reported[3]. A clear difference is that, as the composition approaches stoichiometric, CTPB propellent becomes more stable and plastic propellent becomes less stable. It has been observed[8], with an AP/PBAA propellent system, that the most fuel-rich propellent has the highest acoustic response. One might expect that as the energy content of the propellent is increased so

would its tendency to instability, but apparently this is not so with elastomeric propellents. The reason for the dissimilarity between the elastomeric and plastic types of propellent is not clear but it may be due to a difference in the structure of the diffusion flame.

Plastic and CTPB propellents may be readily compared in Figs.4 and 5 where the acoustic responses and maximum pressure amplitudes are shown against frequency for a series of propellents in which the oxidizer/fuel ratios were varied. The range of acoustic response is only slightly lower for the CTPB propellents but the range of maximum pressure amplitude is appreciably lower than for the range of plastic propellents. It is deduced that, without additives, CTPB is a more stable propellent system. Titanium dioxide, frequently added to plastic propellent to stabilize combustion, reduces the acoustic response by about 50% and the maximum pressure amplitude one hundredfold.

An important observation is the markedly lower acoustic pressure amplitude for CTPB propellent compared with that for plastic propellent, although the difference between the acoustic responses is small. During the growth period of the acoustic oscillations the gain clearly exceeds the losses. However, a steady pressure amplitude is attained when two conditions prevail:

(i) the sum of the acoustic losses equals the acoustic gain,

(ii) with respect to pressure amplitude, the rate of increase of acoustic loss exceeds the rate of increase of acoustic gain.

There is a single source of acoustic gain, namely the energy release in the burning zone. In the T-burner there are three main sources of acoustic loss:

(a) visco-thermal and molecular relaxation in the gas phase,

(b) visco-elastic damping in the propellent itself,

(c) thermal losses through the burner case.

The change in fuel from PIB to CTPB gives only a small reduction in acoustic response and the difference in gas-phase damping between the two groups of propellent is only marginal, as determined by measurements of the decay constants of the pressure oscillations immediately after propellent burnout. Therefore, it seems reasonable to deduce that the visco-elastic damping in the CTPB propellent is greater than that in PIB propellent and accounts for the greater absorption of acoustic energy. A second possibility is that differing kinetics of the decomposition of PIB/AP and CTPB/AP propellents are

causing differing phase lags between μ and ε, resulting in the imaginary parts of the acoustic response being different.

4.3 Addition of ferric oxide to CTPB propellent

A comparison of propellents C 53/1 and C 48/2 in the table shows that 1% ferric oxide increases the propellent burning rate by about 20%. This increase of burning rate is commonly observed when iron compounds are added to CTPB propellents.

The effect on combustion stability is seen in Figs.1 and 3. The propellent containing 1% ferric oxide has a somewhat greater acoustic response and maximum pressure amplitude at higher frequencies, 3 - 4 kHz, than the uncatalysed propellent, whereas at the lower frequencies, 0.7 - 3 kHz, there is little obvious difference. This again contrasts with the results found for plastic propellent, where an additive which increased the burning rate (e.g. TiO_2, SiO_2, $CuCrO_4$) decreased both the acoustic response and the maximum pressure amplitude. The reverse effect has been observed when LiF is an additive.

These results show quite clearly the difficulty in predicting the stability characteristics of propellents and the necessity for examining all new propellents.

4.4 Correlation between instability and propellent burning rate

A distinct correlation was found for plastic propellent between the propellent burning rate, the acoustic response and the maximum pressure amplitude sustained in the T-burner[9]. The data for the four CTPB propellents used in this work have been included in these correlations in Figs.6, 7 and 8. Figs.6 and 7 demonstrate that for the particular burning rate range 9 - 13 mm sec^{-1} the CTPB propellents have the greater stability. However other CTPB propellents are to be studied to determine whether this enhanced stability is applicable for a wider range of burning rates. The comparatively greater stability of CTPB propellents over plastic propellents, mentioned in 4.2, is clearly shown in Fig.8 where the maximum pressure amplitude associated with a particular acoustic response is plotted for two different frequencies. The maximum pressure amplitude for a particular acoustic response is lower for the CTPB propellents than for the plastic propellent. Possible reasons for this have been suggested in 4.2.

4.5 Comparison with other studies on CTPB propellents

Brown et al.[4,5,6] have studied the effect of several additives and of coating the oxidizer particles in a CTPB/AP propellent with polymeric materials. The results from this present work at the R.P.E. cannot be readily compared with those of Brown because he used a more fuel-rich propellent, containing 22% binder/78% oxidizer and the majority of his results were obtained at a mean pressure of 1.379 MN/m^2 (200 psi) with a few at 3.447 MN/m^2 (500 psi). The R.P.E. work was carried out at a mean pressure of 6.894 MN/m^2 (1000 psi), chosen as representative of our solid propellent motor operation.

5 CONCLUSIONS

The following are the principal conclusions to be drawn from this work.

(1) The most fuel-rich CTPB propellent is the least stable, whereas the two less fuel-rich CTPB propellents, which possess less acceptable physical properties (in their low temperature limit), are associated with more stable combustion.

(2) Addition of 1% ferric oxide to CTPB propellent causes a small decrease in stability at the higher frequencies (3 - 4 kHz). The effect at lower frequencies is negligible.

(3) CTPB propellent shows greater stability of combustion than plastic propellent which contains no ballistic modifier. However plastic propellent containing an additive such as TiO_2 or SiO_2 has a similar combustion stability to that of CTPB propellent. The present work shows that for the range of burning rates, 9 - 13 mm sec^{-1}, CTPB propellent is more stable than those plastic propellents so far investigated.

(4) The maximum pressure amplitude associated with a given acoustic response is less for CTPB propellents than for plastic propellents. It is suggested that this may be caused either by greater absorption of acoustic energy by CTPB propellents or by different reaction kinetics causing differing time lags between the perturbation caused in the burning rate by a perturbation in pressure. Experiments are planned to investigate these suggestions.

ACKNOWLEDGEMENT

The author would like to thank Mr. J. Scrivener of the E.R.D.E. for his suggestions and for providing the special propellent samples.

Table

COMPOSITIONS AND SOME BALLISTIC PROPERTIES OF THE CTPB PROPELLENTS

Propellent	Composition, per cent by weight					Ratio oxidizer/ polybutadiene rubber	Linear burning rate at 6.894 MN/m^2, r, mm/sec	Flame temperature, ^oK	Theoretical specific impulse, 1000 to 14.7 psi, lbf sec/lbm
	Ammonium perchlorate*	Carboxy-terminated polybutadiene rubber	Isodecyl pelargonate	Ferric oxide	Iron lineoleate				
C 50/12	84	14	2	0	+0.1	6.00	9.4	2716	240.1
C 53/1	86	12	2	0	+0.1	7.17	10.3	2894	245.5
C 54/1	88	10	2	0	+0.1	8.80	10.8	3013	249.8
C 48/2	85	12	2	1	+0.1	7.08	12.5	2849	242.4
ϕ	90.08	7.92	2	-	-	11.37	-	3012	251.2

* The ammonium perchlorate is a 50/50 mixture of BS 10–60 mesh and $S_0 = 2000\ cm^{-1}$.

ϕ This propellent is stoichiometrically balanced to CO_2, H_2O and HCl.

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No.	Author	Title, etc
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9	R.D. Gould	Combustion instability studies with plastic propellent. A.I.A.A. Preprint 69-478 (1969) R.P.E. Technical Memorandum 500 (1969)

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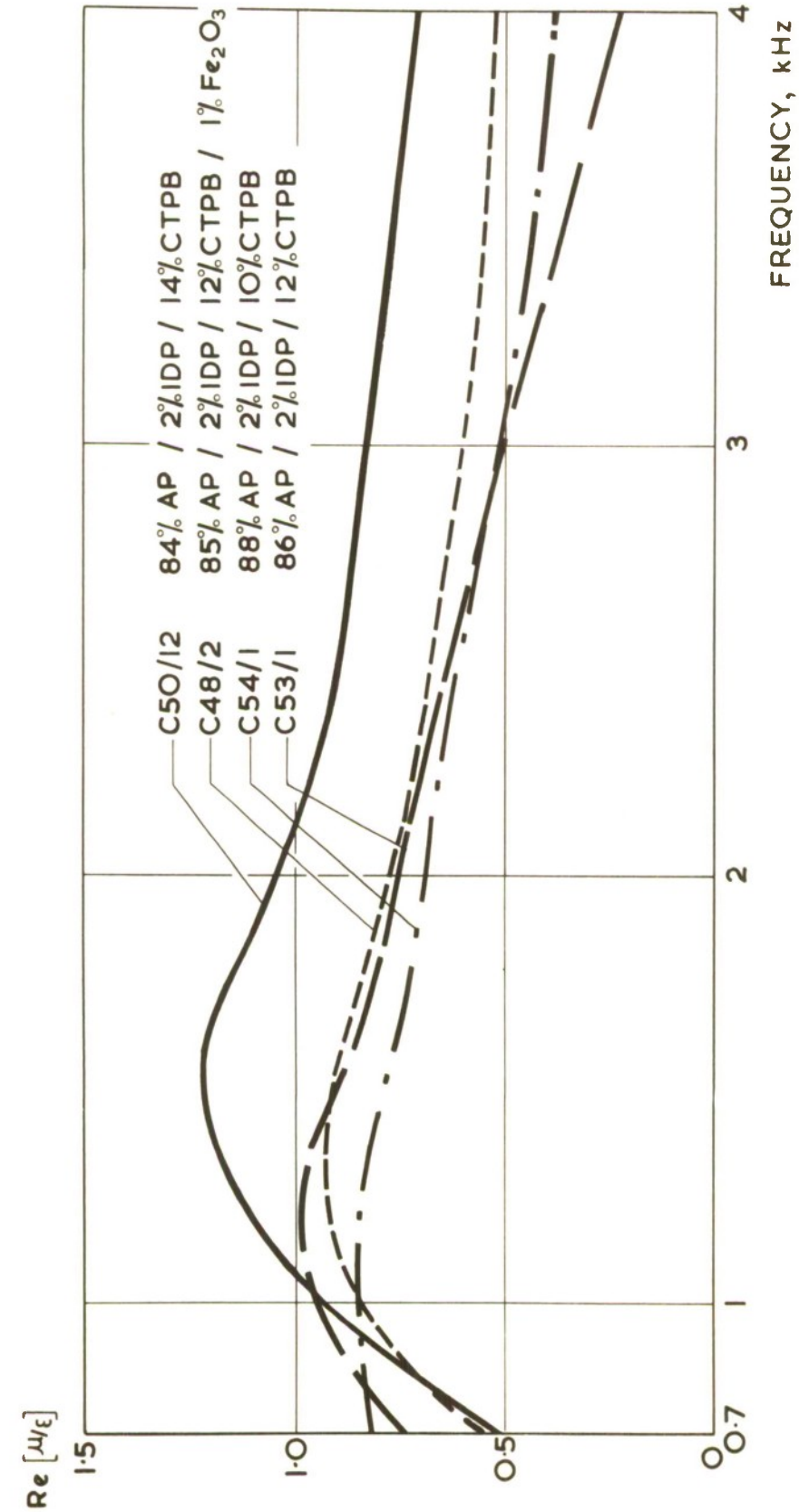

FIG.1 ACOUSTIC RESPONSE OF FOUR CTPB PROPELLENTS

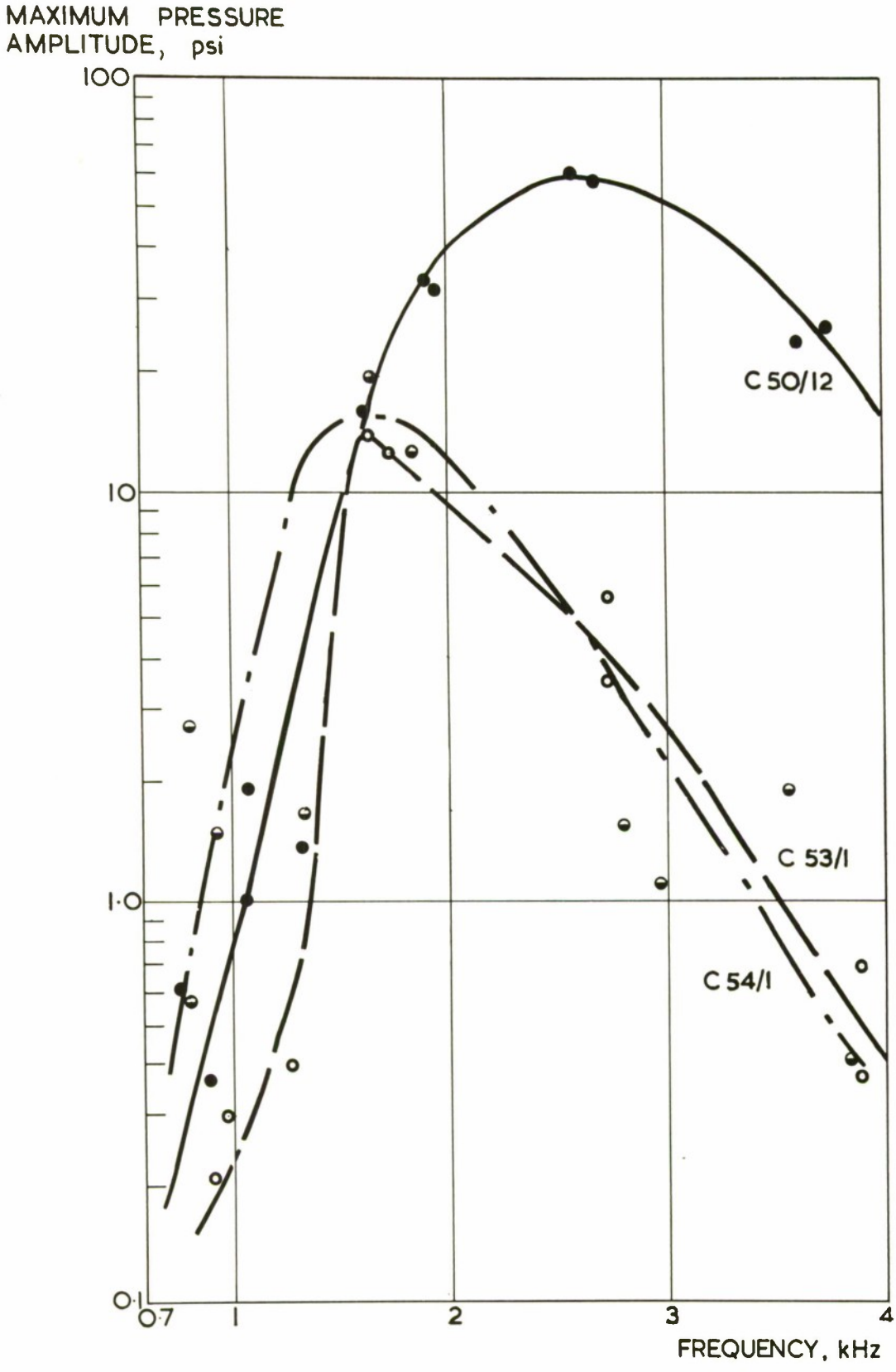

FIG. 2 EFFECT OF OXIDIZER FUEL RATIO ON MAXIMUM PRESSURE AMPLITUDE REACHED IN T-BURNER

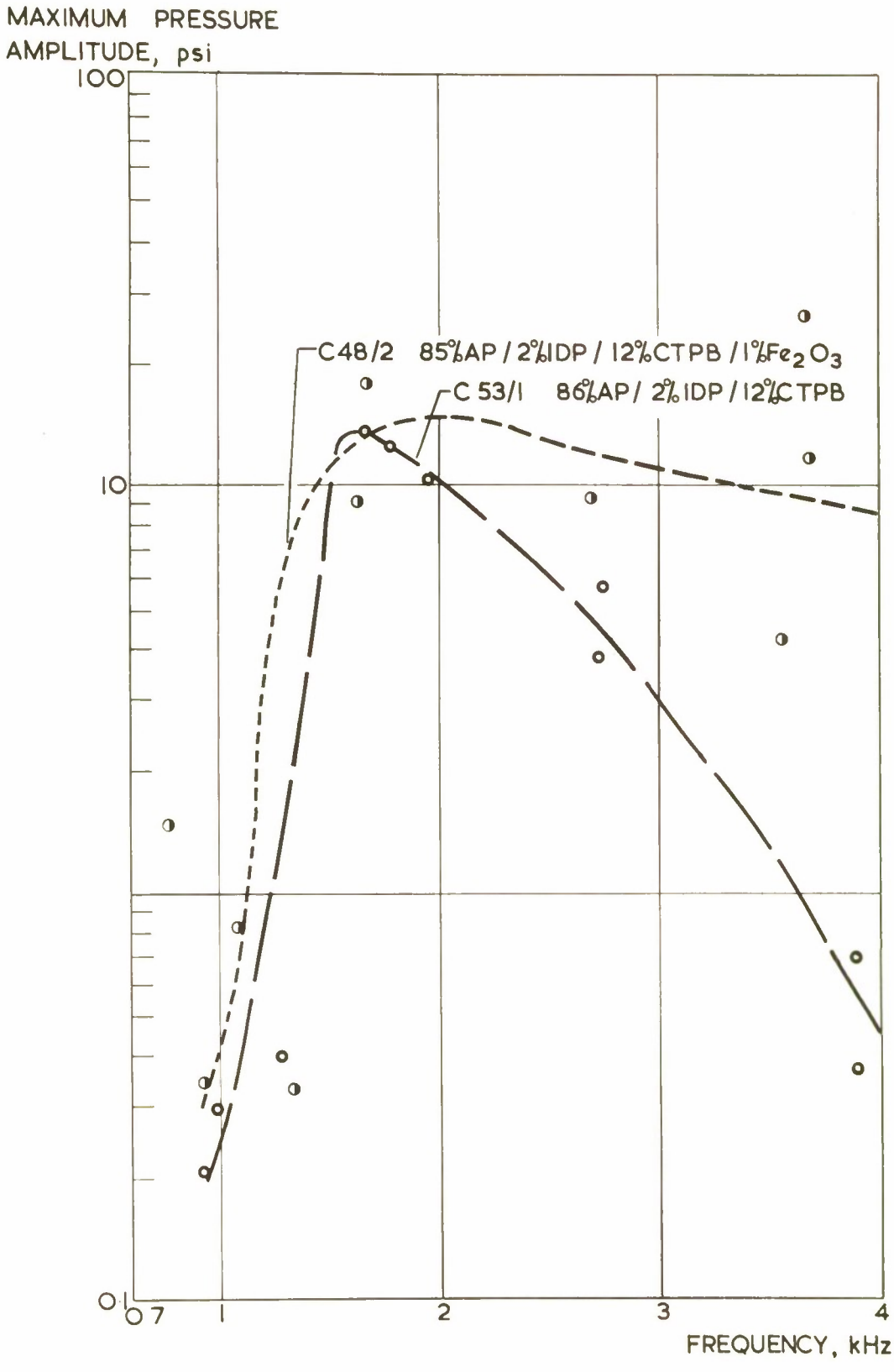

FIG. 3 EFFECT OF 1% FERRIC OXIDE ON MAXIMUM PRESSURE AMPLITUDE REACHED IN T-BURNER

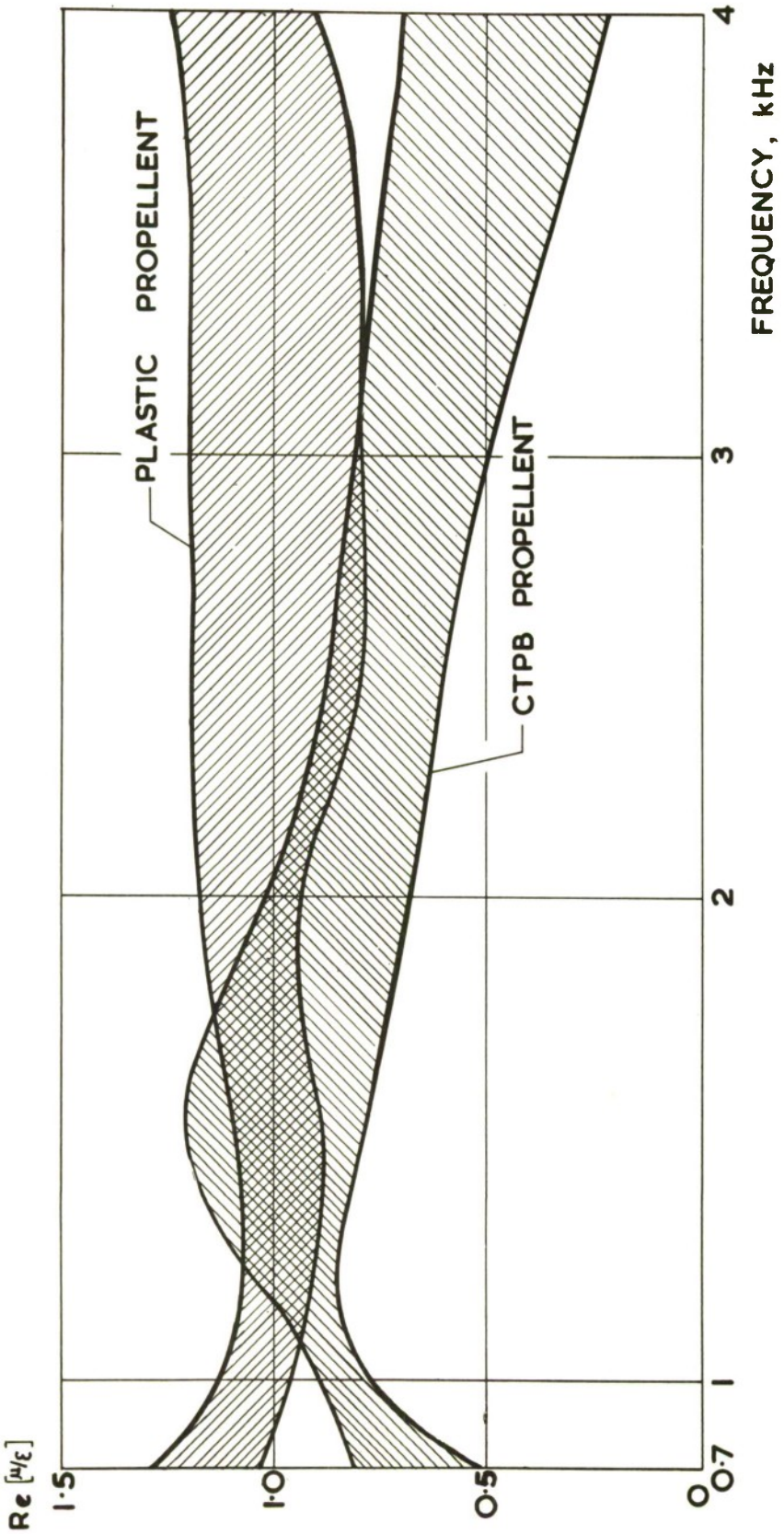

FIG. 4 A COMPARISON OF THE ACOUSTIC RESPONSE OF PLASTIC AND CTPB PROPELLENTS

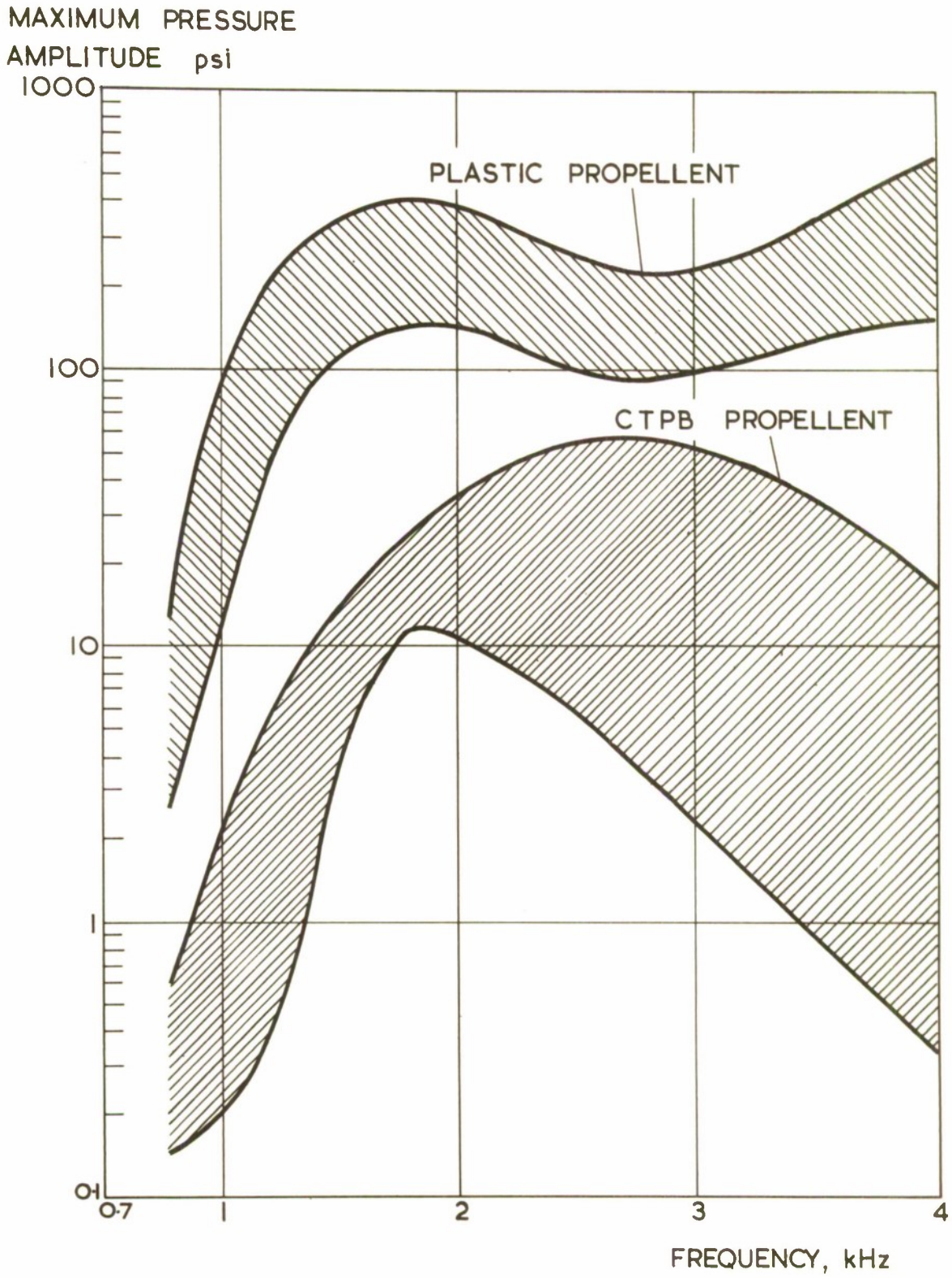

FIG. 5 A COMPARISON OF THE MAXIMUM PRESSURE AMPLITUDE REACHED IN THE T-BURNER BY PLASTIC AND CTPB PROPELLENTS

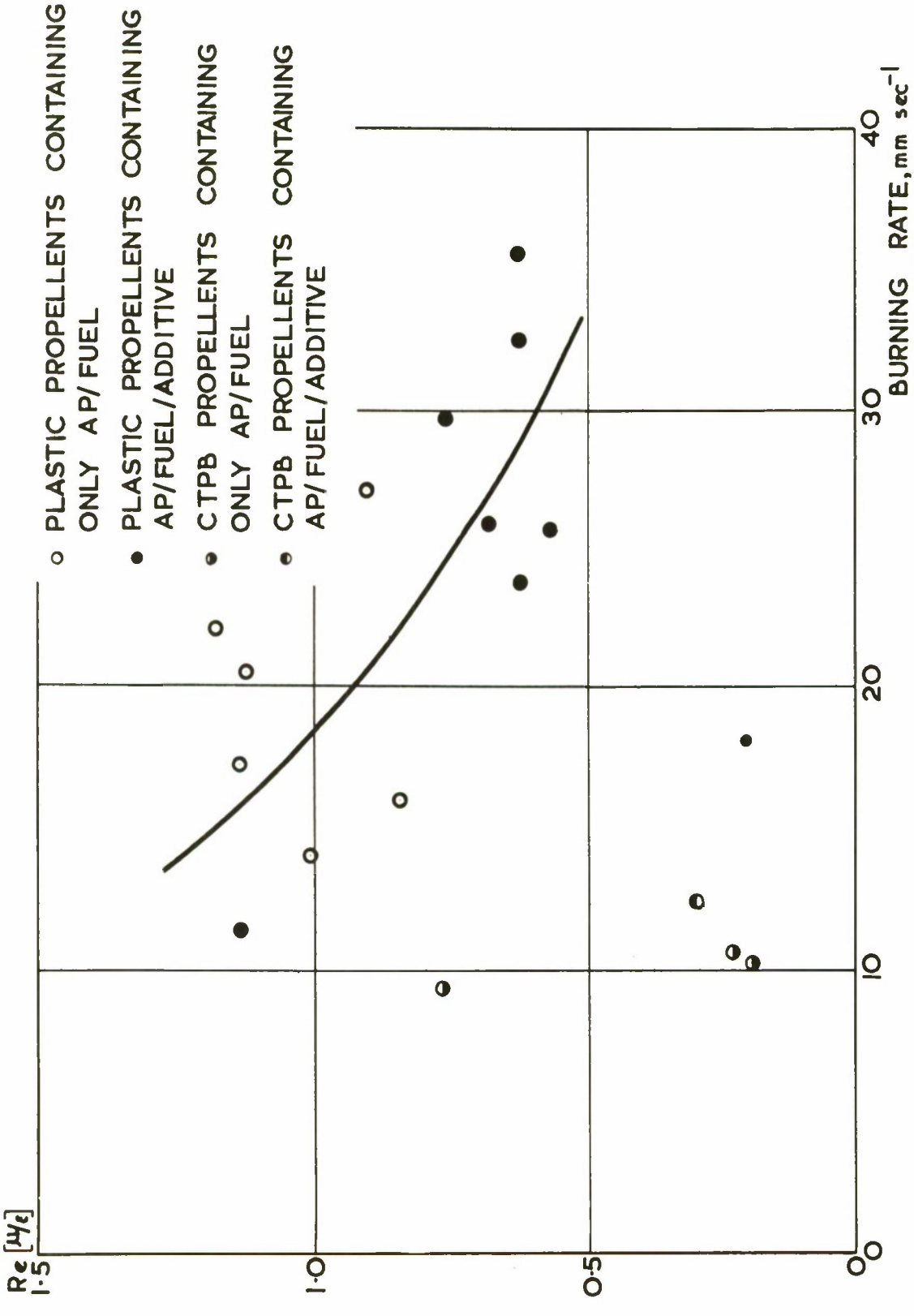

FIG.6 ACOUSTIC RESPONSE AT A FREQUENCY OF 3·5 kHz AS A FUNCTION OF PROPELLENT BURNING RATE

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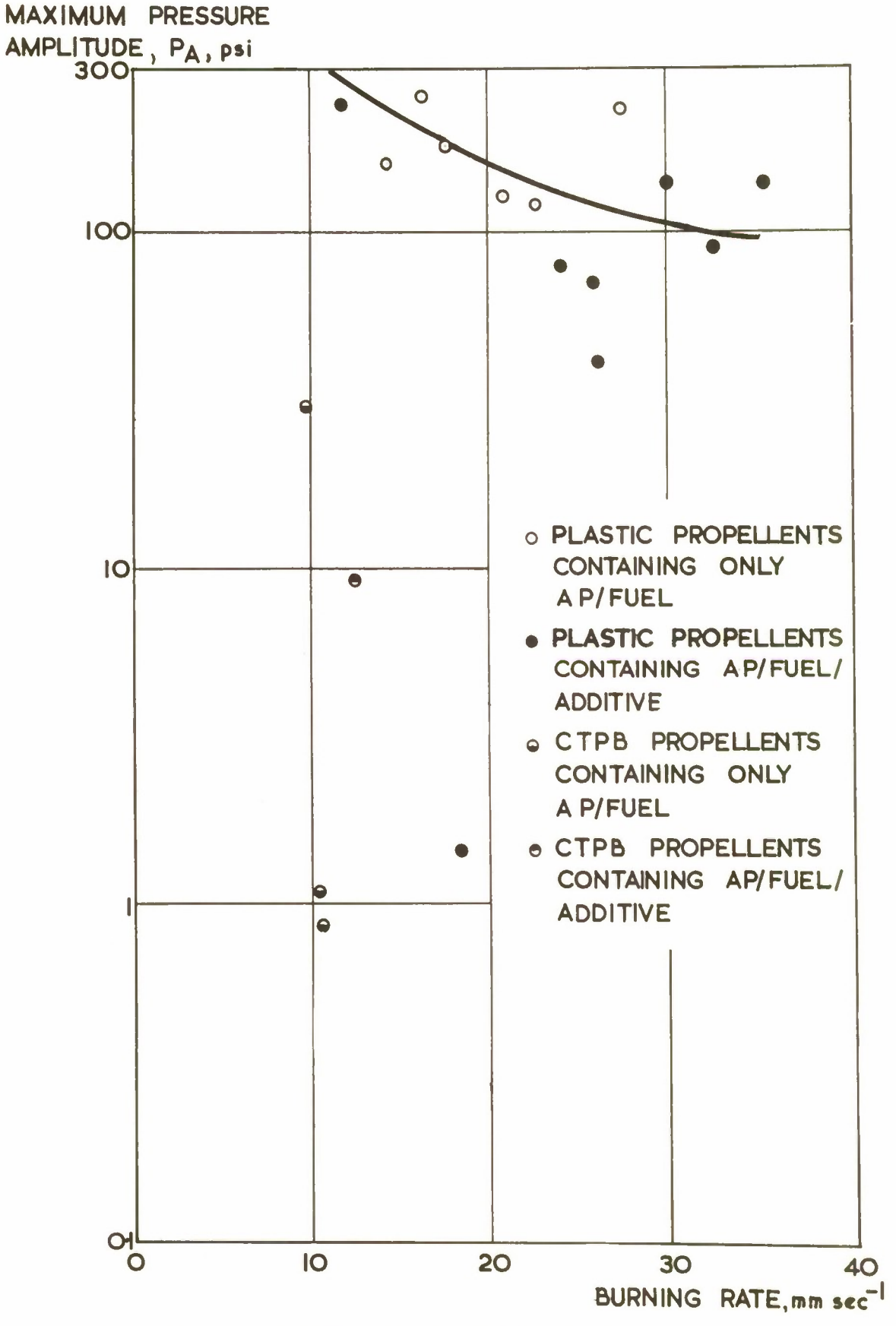

FIG.7 MAXIMUM PRESSURE AMPLITUDE AT A FREQUENCY OF 3·5kHz AS FUNCTION OF PROPELLENT BURNING RATE

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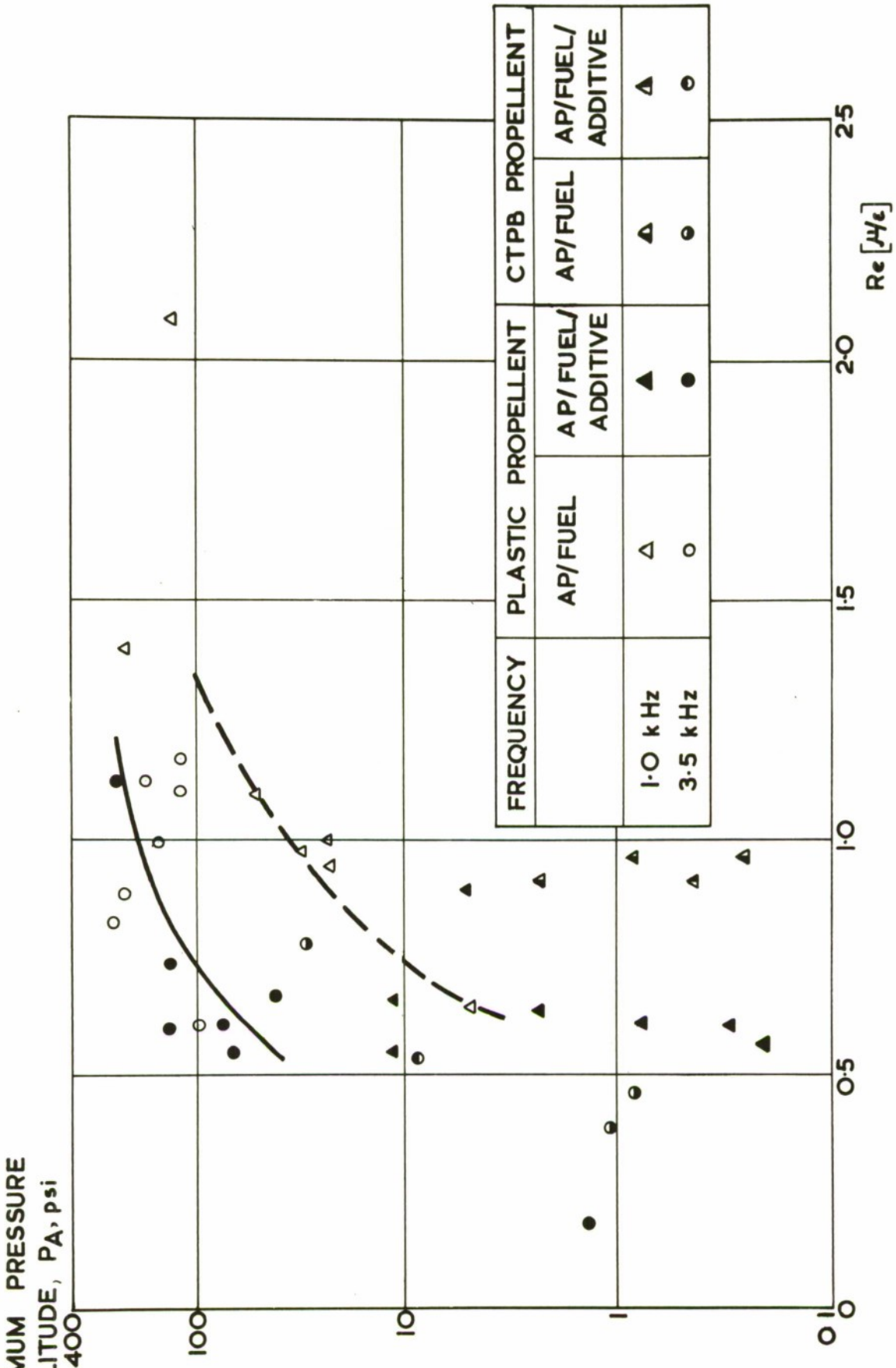

FIG.8 MAXIMUM PRESSURE AMPLITUDE AS A FUNCTION OF ACOUSTIC RESPONSE

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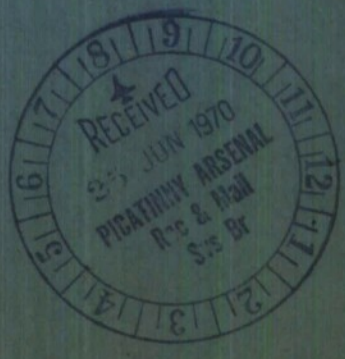

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