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THEORETICAL INVESTIGATION OF EROSIVE BURNING OF SOLID PROPELLANTS

by

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University of Brussels
Belgium

TECHNICAL ~~NOTE NR. 3.~~ REPORT

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Abstract.

After a critical survey of existing theories of erosive burning and of published experimental data, the combustion mechanism of ammonium perchlorate propellants is discussed and a model of erosive burning of these formulations is proposed.

Erosion is assumed to smooth the surface whose burning rate is then controlled by oxidizer regression, no energy being supplied by the main diffusion flame. Furthermore the adiabatic decomposition temperature of the perchlorate is assumed to be obtained at the end of the laminar sublayer whose thickness can be related to mean flow velocity through fluid dynamics. Correlation of test data permits to determine the transition point. Grain design and motor scale are taken into account through local hydraulics radius.

Low pressures, large radii and high burning rates are shown to reduce erosive burning.

Finally an attempt is made to explain irregular burning by surface nature and roughness, through erosivity.

TABLE OF CONTENTS.

	Pages.
- Abstract	i
- 1. INTRODUCTION	1
- 2. SURVEY OF EXISTING THEORIES OF EROSIVE BURNING.	4
A. The Lenoir - Robillard Theory.	4
B. The Corner Theory and its Developments.	5
α Corner.	5
β Boisson and Tavernier.	6
γ Geckler.	7
δ Vandenkerckhove.	9
- 3. EXPERIMENTAL DATA.	11
A. Burning Rate.	11
B. Influence of Grain Design and Motor Scale.	14
C. Experimental Techniques.	21
- 4. THEORETICAL STUDY OF EROSIVE BURNING OF AMMONIUM PERCHLORATE PROPELLANTS.	25
A. Burning Mechanism of Ammonium Perchlorate Propellants.	25
B. Erosive Burning of Ammonium Perchlorate Propellants.	32
C. Mathematical Model of Erosive Burning.	40
α Solid-Phase Decomposition.	40
β Heat Transfer across the Decomposition Zone.	40
γ Fluid Dynamics.	44
δ Numerical Application.	47
- 5. INFLUENCE OF GRAIN DESIGN AND MOTOR SCALE.	55
- 6. A TENTATIVE EXPLANATION OF IRREGULAR BURNING IN SOLID PROPELLANT ROCKETS.	60

1. INTRODUCTION.

Experimental data show that the burning rate of a solid propellant is increased above its normal pressure-dependent value by the presence of a flow parallel to the burning surface.

This phenomenon, which plays an important role in internal ballistics of high performance rockets, is known as EROSIVE BURNING.

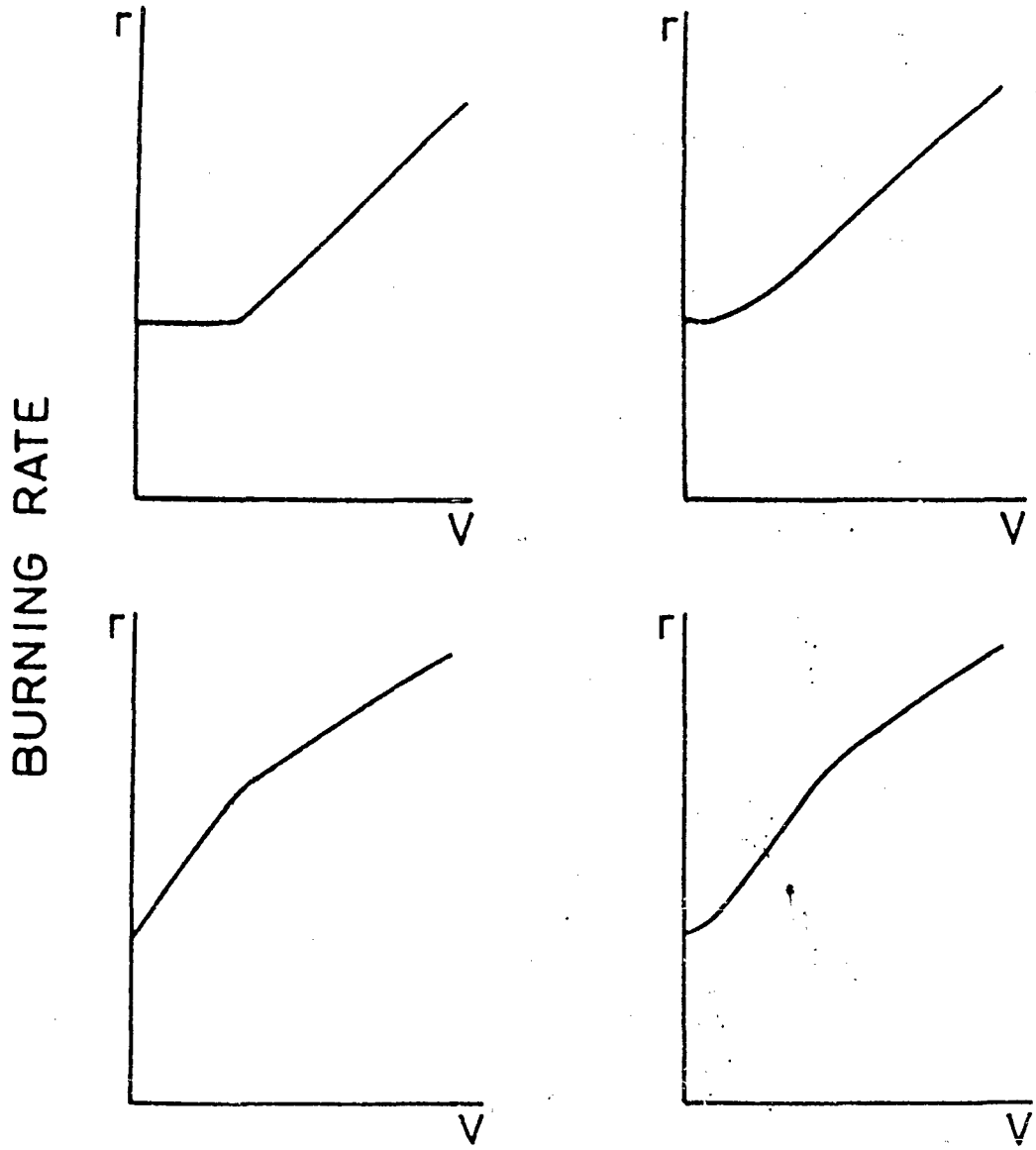
Its existence has been recognized early in the developmentt of solid propellent motors. Despite several important contributions, however, it has not deserved much attention until recently, since it has been possible to overcome rather easily by cut and try its major detrimental effects on relatively small-sized motors.

The cost of firing the very large solid propellant rockets presently in the development phase precludes this empirical approach.

Moreover the method permits to overcome only the most obvious disadvantages resulting from erosive burning, such as the appearance of a pressure peak after ignition, or burnthrough due to uneven combustion along the grain length and premature contact of the hot gas with the chamber wall at the nozzle entrance where the flow velocity is a maximum.

The most severe difficulty in studying these phenomena is the absence of a sufficient volume of reliable and systematic experimental information which results in representing erosive burning by means of oversimplified relationships which barely fit the data for one propellant but do not even describe the behaviour of another similar formulation. These empirical relationships, which assume linearity between burning rate increase and flow velocity, Mach number, mass velocity or reduced mass velocity, may rather satisfactorily represent the phenomenon under severe erosive conditions. In most cases, however, they appear to be insufficient to predict the burning rate under conditions of lean erosion, even if the existence of a controversial "threshold velocity" is taken into account.

In fact the analysis of available data suggests that the burning rate dependence on flow velocity, Mach number, mass velocity or reduced mass velocity can exhibit many patterns , depending on propellant formulation and somewhat on combustive pressure. Figure 1 represents four possibilities which can be encountered.



FLOW VELOCITY, MACH NUMBER, MASS VELOCITY or REDUCED MASS VELOCITY

FIG.1

Closer analysis shows that the burning rate without erosion $_o$ appears more or less as an anomaly. Under strong erosion it is doubtful that the parameters a and n of the classical law:

$$r_o = a\,p^n$$

still play a predominant role.

Any empirical relationship giving the total burning rate r, including erosion effect, in terms of r_o is, therefore, suspicious, even if its use appears to provide valuable results. This point of view has been developed in a previous report dealing with the influence of erosive burning on internal ballistics [1] .

Prediction of the influence of such factors as grain geometry and scale or minor changes in formulation on erosive burning could only be achieved through a fair physical understanding of the phenomenon, taking into account the combustion mechanism of the propellant.

Moreover an improved understanding of the burning mechanism and of the erosivity may provide a tentative explanation for unstable combustion in solid propellant rockets.

Despite years of intensive research by many groups, these problems are still barely understood : the speculative nature of the present work is thus plainly realized by the author. Indeed, over and above several drastic assumptions, the theory developed hereunder is entirely based on a simplified combustion mechanism on which a rather rough fluid mechanics model has been superposed for taking into account erosive burning. The combination of these two theories, however, provides some interesting possibilities for cross-checking the assumption with the experimental results; by all means this type of frontal approach is the only possible one for progressing towards the understanding of the phenomena.

X X X

In this report, special emphasis has been given to the case of composite propellants using ammonium perchlorate as oxidizer, in view of their wide range of application.

2. SURVEY OF EXISTING THEORIES OF EROSIVE BURNING.

This survey does not intend to describe in details the mathematics of the various theories which have been proposed for explaining erosive burning, but rather to discuss the hypothesises on which these models are based.

All these theories neglect the mechanical effects of flow on the propellant and assume that the increase in burning rate results from accelerated chemical reactions under the influence of some mechanism of fluid dynamics. These theories can be divided in two broad categories depending on whether the flame structure is taken into account or not.

A. The Lenoir - Robillard Theory.

The best known theory of erosive burning of solid propellants has been proposed by Lenoir and Robillard [2] . It has also been surveyed by Green, Penner and Schultz who described it as a major advance towards a description of the erosive burning mechanism. [3] .

Lenoir and Robillard have applied an empirical relationship of the type employed by Rannie and others in studies of heat transfer to transpiration-cooled surfaces, under the assumption that the presence of a flow parallel to the surface accelerates the convective heat transfer between the main gas core and the burning surface.

It is believed that this model suffers from a fundamental drawback: the basic relationship used by Lenoir and Robillard describes the heat transfer to transpiration cooled surfaces only when the temperature gradients, in the gas, are due to convection only, while in the presence of a burning surface the temperature gradients are determined primarily by the chemical reactions in the combustion zone, the flow pattern having only a second order influence.

The good numerical results are not an absolute proof of the validity of their model since two constants are computed from experimental data in order to obtain the agreement.

This theoretical objection is supported by the observations of several authors who reported that erosive burning is not influenced by the temperature of the main gas flow [4, 6, 7, 14] , and even, in certain cases under sufficiently strong erosive conditions, by the combustion temperature of the propellant itself [14] .

The theory proposed by Lenoir and Robillard has been used successfully for explaining such behaviours as the inverse dependence of the erosive effect upon propellant burning rate or the controversial existence of an apparent velocity threshold near the fore end of the grain.

We believe, however, that this success is due to the fact that only a few cases of practical importance have been studied without attempting a systematic investigation of the phenomenon in the full range of pressure, formulation, granulation or scale.

B. The Corner Theory and its Developments.

As pointed out above, the burning rate is primarily determined by chemical reactions and erosion introduces a second order effect only. A theory of erosive burning must, therefore, take into account the flame structure and describe how it is affected by fluid dynamics. Such a frontal approach is, basically, difficult since it involves the coupling between two phenomena which , even separately, are barely understood i.e. the combustion mechanism and the flow field.

a Corner.

The first approach along these lines is due to Corner [4].

After having remarked that near the aft end of the charge, under severe erosion, typical values of the Reynolds number range from 10^5 to 10^6, this author used the Prandtl-Karman momentum theory for representing the boundary layer and for computing, within the combustion zone, the increase in thermal conductivity which is introduced by turbulence, above the laminar sublayer.

This approach gives the effective thermal conductivity which takes into account eddy diffusivity, as a function of the distance from the burning surface as well as the mean flow velocity in the section under consideration.

Therefore it should be possible, in principle, to integrate the equations describing the combustion, with a variable conductivity, at the price of a considerable increase in complexity.

Alternatively a suitable mean value of the distance from the surface might be selected that would give a mean conductivity applicable in the most important region of the flame. Corner selected the distance at which the reaction is half completed without erosion, an assumption which does not take into account the fact that this characteristic distance almost certainly decreases as the mean flow velocity increases.

Altough no serious attempt was made to draw systematically quantitative results, Corner's theory provides a good explanation for the following experimental facts:

- slow burning propellants are more sensitive to erosion than fast burning ones which are characterized by thinner flames,
- erosive burning is insensitive to the temperature of the main flow since the surface is bathed in its own products and these are set into transverse motion by the main stream,

- the threshold velocity below which erosion does not increase the burning rate is due to the penetration of turbulence in the combustion zone.

Two major objections, however, can be drawn against Corner's approach.

First, from the point of view of fluid mechanics, even its limited success appears remarkable since it is based upon empirical expressions for the velocity distribution in a one-dimensional flow adjacent to an inert boundary and the effects of mass addition normal to the stream are not considered. This type of one-dimensional approximation would be expected to yield a reasonably accurate representation of the actual flow field only near the aft end of the grain where the ratio of normal injection velocity to main-stream velocity is low, of the order of 0.01 [3] .

Furthermore the one-dimensional velocity distribution is valid only under the assumption of a fully developed turbulence for which the characteristic dimension in the Reynolds number is the pipe diameter. In internal ballistics the length to diameter ratio of the perforation is seldom sufficiently large for neglecting the two-dimensional nature of the flow field which is influenced by the distance from the fore end of the grain.

Secondly Corner assumed that the rate controling step of the combustion is the main gas phase reaction. This may be a realistic assumtion at the very high pressures encountered in guns, above 1.000 kg/cm^2. In the normal pressure range used in rocket motors, below 100 kg/cm^2, it is generally agreed that the rate controlling step is the solid-phase decomposition governed by the combustion surface temperature T_s through an Arrhenius type relationship.

Furthermore the structure of the flame is rather complex and in many cases several zones can be distinguished.

β - Boisson and Tavernier.

In an attempt to correlate the experimental data obtained by Berger, Prache and Tavernier [5] , Boisson and Tavernier extended the Corner theory for taking into account the mass-diffusion due to turbulence, in addition to the increase in thermal conductivity [6, 7] . These authors concluded that in the low pressure range, the turbulent mass-diffusion has a predominant influence on erosive burning. No attempt has been made, however, for systematically exploring the quantitative influence of the various parameters.

Although Boisson and Tavernier contributed to the physical understanding of erosive burning by emphasizing the importance of turbulent mass-diffusion in the reaction zone, their theory suffers from the same drawbacks as the Corner theory: the fluid mechanics model is oversimplified and, moreover, the assumption of a main gas reaction controling the burning rate does not appear realistic in the low pressure range.

Y - Geckler.

The first serious attempt to take into account the flame structure for computing the erosive burning constant is due to Geckler. [8].

In his famous survey about combustion mechanisms of solid propellants this author adapted the Corner theory for taking into account the flame structure of double base propellants which has been developed by Parr, Crawford, Rice and Ginell. According to this model, the rate controling step of the combustion is the solid-phase decomposition which is governed by an Arrhenius-type equation, and the gas-phase reaction can be divided in three parts. Close to the surface exothermic reactions take place in the fizz zone. Then, in the preparation zone, activated products are formed without heat production. Finally, when a sufficient concentration of activated products is achieved, the final reaction occurs in the combustion zone at the end of which the isobaric combustion temperature is obtained (figure 2). Furthermore these authors have shown that at sufficiently low pressure, below 100 atm, the thickness of the preparation zone is much greater than the thickness of the other zones, and the heat transfered from the flame zone into the fizz zone can be neglected. Geckler thus selected the thickness y_1 of the fizz zone as the suitable mean value of the distance from the surface representing the most important region of the flame.

Using for y_1 the values obtained by Rice and Ginell, Geckler computed for that particular distance, through the Prandtl-Karman momentum theory, the effective thermal conductivity taking into account the turbulent term and applied the result to Corner's equation:

$$\frac{r}{r_o} = \left(\frac{\lambda'}{\lambda}\right)^{0.5}$$

with r the actual rate under erosive conditions,

r_o the corresponding burning rate without erosion

λ the thermal conductivity without turbulence,

and λ' the effective thermal conductivity at distance y_1 taking into account turbulence.

In applying this method to propellant HES 4016 which has been studied in great details by Rice and Ginell, Geckler obtained an extraordinary good agreement with the experimental data. He remarked, however, himself that although remarkable, this agreement is probably fortuitous. Indeed, from the fluid mechanics point of view, this treatment suffers from the same drawbacks as Corner's theory discussed previously. Furthermore, the preceding relationship has been established by Corner in the assumption of a gas-phase reaction controlling the burning rate. This is not consistent with the assumption of the solid-phase decomposition control of the burning rate which has been emphasized through Geckler's survey. Nevertheless this author remarked that this equation provides a reasonable approximation. For checking its validity, we made a rough calculation which seems to indicate that the exponent 0.7 may be more realistic than 0.5.

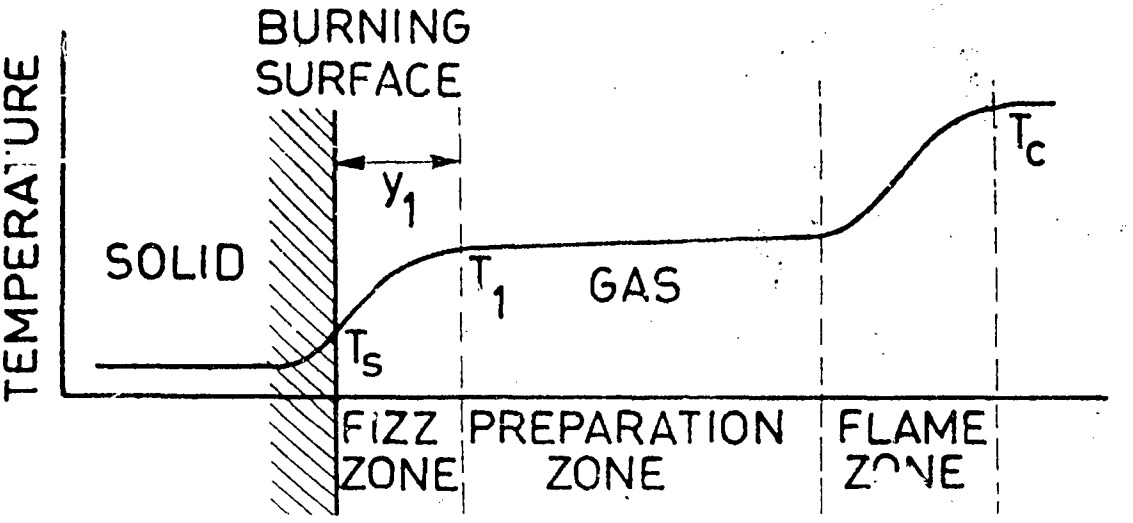

BURNING
SURFACE
TEMPERATURE
SOLID
y_1
T_1
GAS
T_s
T_c
FIZZ
ZONE
PREPARATION
ZONE
FLAME
ZONE

FIG. 2

Finally, Geckler remarked that this theory suffers from the drawback of not taking into account the decrease in the fizz zone thickness which results from an increase in burning rate due to erosion.

δ - Vandenkerckhove.

In attempting to improve the theory further, Vandenkerckhove proposed a complex model of erosive burning based on rather controversial phenomenological assumptions, which give fair quantitative results [9]. After having established the general heat transfer equation across the fizz zone of a double base propellant, for the purpose of relating the surface temperature T_s to the zone thickness y_1 and to the temperature T_1 reached at the end of the zone, he remarked that this relationship is valid in the laminar boundary layer, even in the presence of a strong velocity gradient parallel to the surface, but that in the turbulent region great caution is necessary.

Nevertheless one can expect that the flame structure still holds in the transition sublayer where turbulence is not yet fully developed and where the dimensions of the eddies are much smaller than the zone thickness.

It seems therefore reasonable to assume that, at least in the low velocity range, temperature T_1 is not significantly influenced by turbulence in the preparation zone across which the heat transfer remains negligible.

Furthermore the influence of turbulence is not only to increase the thermal conductivity by transporting hot gases towards the surface. Hitherto unreacted products are also transported back in the process in such a manner that they will react closer to the surface. Vandenkerckhove thus assumes that inside the fizz zone temperature T_1 is exactly reached at the limit of the laminar sublayer. The heat transfer equation therefore, relates the surface temperature, and thus the burning rate, to the thickness of the laminar sublayer which depends on mean flow velocity through fluid dynamics considerations.

Like Corner, he approximated the flow pattern in the perforation by the well known theory of pipes, in which, for sufficiently large Reynolds numbers, the transition from laminar to turbulent takes place at a certain distance y of the surface, characterized by a critical value of the so-called friction distance parameter y^*_{cr}. For pipes, this critical value ranges from 5 to 10. In the problem under consideration, a somewhat different value can be expected, due to the second order effect of mass addition whose velocity, perpendicular to the surface, represents approximately one per cent of the mean flow velocity in the region of interest.

This influence can be taken into account empirically by identifying the threshold velocity U_{tv} which is the mean flow velocity below which no erosion occurs, as the precise velocity for which the thickness of the fizz zone is exactly equal to that of the laminar sublayer.

In the numerical example, for U_{tv} = 180 m/sec, he found :

$$y^*_{cr} = 2.85$$

which appears reasonable.

Above the threshold velocity, turbulence penetrates the fizz zone, thus reducing its effective thermal thickness and accordingly increasing the surface temperature and the burning rate. This increase can be computed easily if it is further assumed that the critical friction distance parameter remains constant.

Despite many drastic assumptions, this theory has been used to compute a value of the erosive constant of JPN which agrees remarkably with experimental data. Over and above this agreement, this work provides a plausible physical explanation for the existence of the threshold velocity which has been observed in several experiences with double base propellants (see figure 3 taken from Wimpress [12] but has also failed to appear in many other tests, especially with composite propellants, and has thus been considered as controversial by many authors (an attempt to explain these different behaviours is made later in this report, in section 4 – B).

This theory still suffers from several drawbacks:

- the influence of mass addition has been taken into account in a most empirical manner while the influence of the distance from the fore end of the grain is still neglected.

- a single example has been computed and, due to the lack of experimental data, no attempt has been made for studying systematically the influence of such factors as burning rate, pressure or perforation dimensions.

- finally the calculation has been based on Rice and Ginell theoretical results obtained for HES 4016 double base propellant, while the values of the threshold velocity and erosive coefficient were those measured for JPN.

Nevertheless the good numerical results were most encouraging despite the great number of parameters whose values were only approximately known.

As for the preceding theories, however, this agreement with experimental data could be fortuitous or could result from parameter value adjustment.

The main purpose of the present report is to check the validity of Vandenkerckhove theory by applying it to composite propellants and especially to formulations based on Ammonium Perchlorate which have never been extensively studied before, despite some preliminary results for Ammonium Nitrate propellants [10, 11].

3. EXPERIMENTAL DATA.

A. Burning Rate.

Figure 3, taken from Wimpress, is typical of the early data obtained for particular propellants without taking apparently into account such factors as pressure or motor scale [12]. In this particular case, for J.P.N., the existence of a threshold velocity is clearly observed.

At our best knowledge, the first systematic experimental study of the phenomenon is due to Green who established the dependence between erosive burning and strand burning rate, for both double-base and composite propellants [13].

These results are summarized by figure 4, the erosion coefficient k_M being defined by the relationship:

$$r = r_c \left(1 + k_M \, G/G^* \right)$$

r_o being the burning rate without erosion, and G/G^* the ratio of actual mass velocity ρV to its critical value, which is a function of MACH Number [1].

The strand burning rate r_o is taken at the standardized pressure of 70.3 kg/cm^2 although the actual measurements have been performed at significantly lower pressure, using a strongly progressive grain (initial inner radius equal to 1.5 cm.). Green, therefore, has not taken into account the influence of pressure on erosion coefficient as well as the existence of the threshold velocity which was unnoticed in most of his tests. These results have also been correlated by Geckler with specific heat ratio and adiabatic combustion temperature in a rather crude manner which does not take into account the influence of ballistic modifiers, oxidizer granulation, or fuel-binder nature [8].

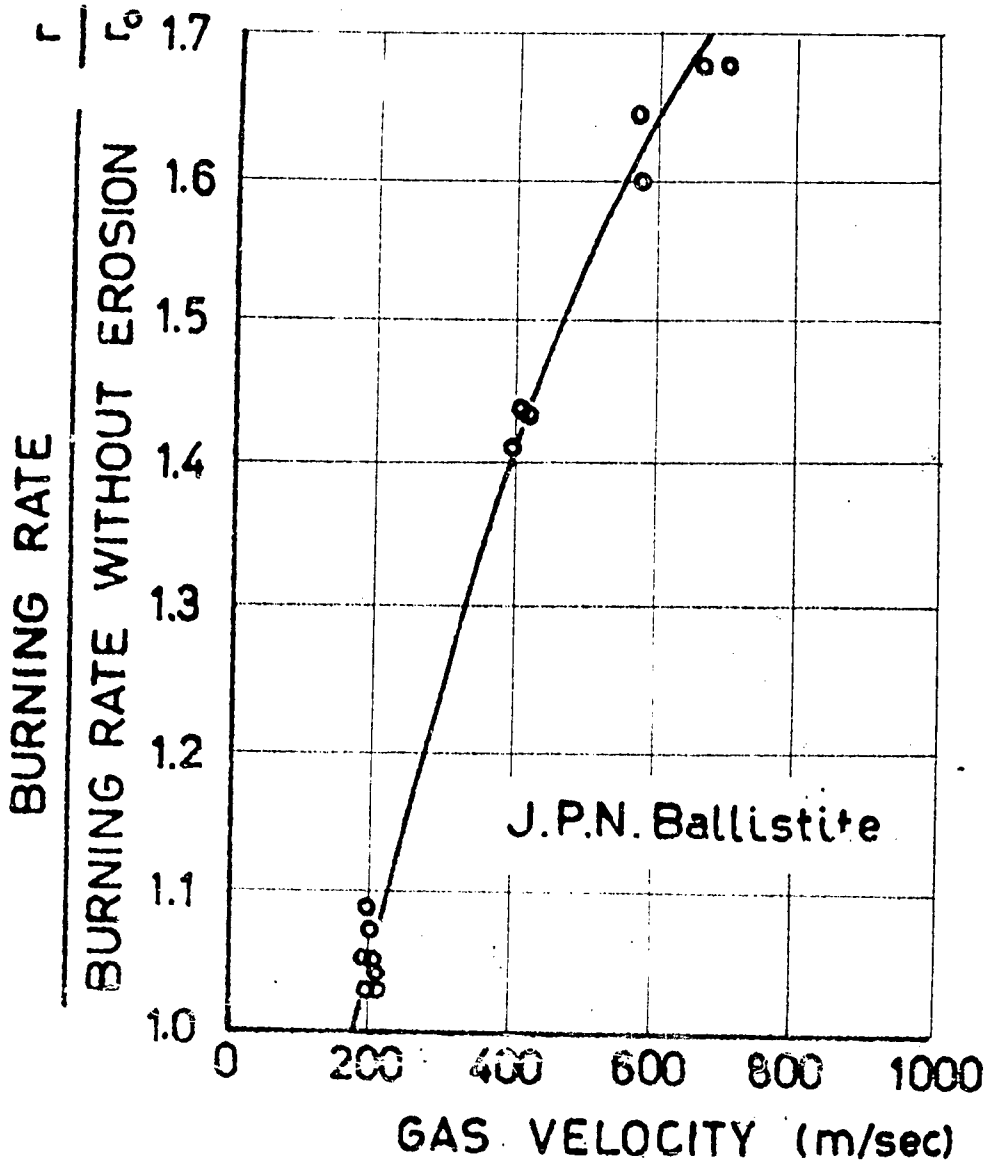

BURNING RATE / BURNING RATE WITHOUT EROSION
r / r₀
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0
200
400
600
800
1000
GAS VELOCITY (m/sec)
J.P.N. Ballistite

FIG. 3

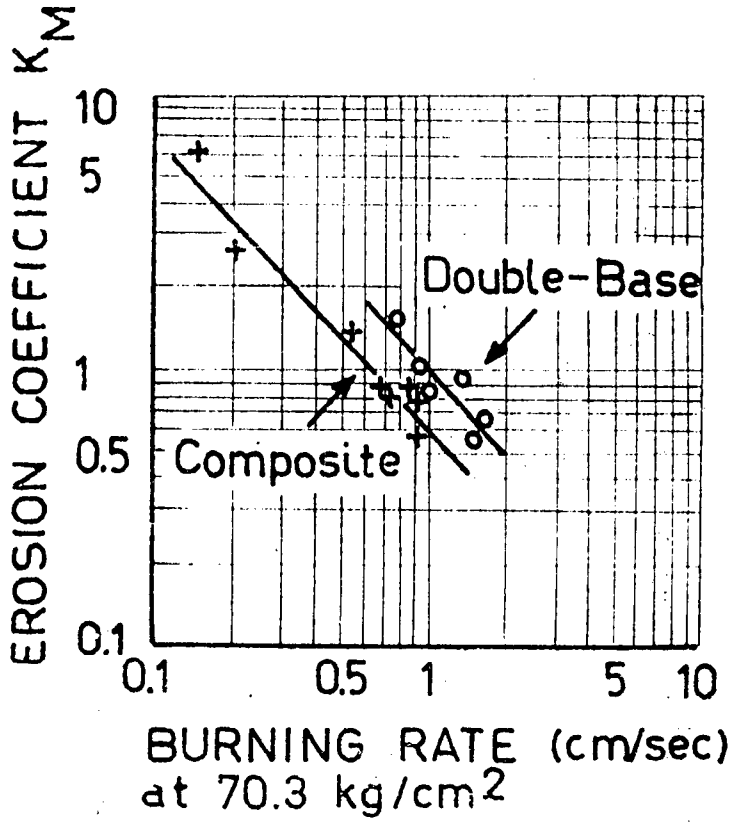

EROSION COEFFICIENT K_M
10
5
1
0.5
0.1
0.1
0.5
1
5
10
Double-Base
Composite
BURNING RATE (cm/sec)
at 70.3 kg/cm^2

FIG. 4

These two references show clearly that fast burning propellants are less sensitive to erosion than slow burning ones.

The best investigation of erosive burning available in the open literature has been performed in Sweden by Lake and Marklund.* [14]. Their results are represented on figure 5 and discussed in details in section 4 - B. It is seen that for a sufficiently strong erosion (for $G/G^* > 0.2$) the severity of erosive burning increases significantly with pressure as shown by figure 6 which gives $\frac{dr}{dG/G^*}$ as a function of pressure.

Marklund has recently obtained new and still unpublished results with both pure ammonium perchlorate and composite propellants [15]. These tests in general confirm our theoretical analysis (see section 4).

X X X X

An increase in burning rate is not necessarily always associated with erosive burning; in fact some tests suggest that for small erosive velocities, below 50 m/sec, the burning rate of certain composite formulations may be slightly decreased below r_o [13, 14] . This phenomenon is still unexplained; it may perhaps just be a secondary effect of the experimental technique.

On the other hand, Price indicated that the so-called mesa double base propellants usually exhibit decreases in burning rate during oscillatory burning [16] . This observation suggests that similar decreases may result from erosive bruning.

B. Influence of Grain Design and Motor Scale.

Experimental evidence shows that erosive burning is also influenced by grain design and possibly by port dimension.

In an attempt to correlate the erosive coefficient k_M with grain design, Fenech and Billheimer introduced a configuration factor χ which is a measure of grain complexity:

$$\chi = \frac{A_c}{A_p} = \frac{S^2}{4\pi A_p}$$

A_c being the flow area of a circular perforation having the same perimeter S than the actual port whose area is A_p [17].

It is believed that a similar investigation is described by Saderholm in a Thiokol special report, "Erosive Burning Study of TP - H 8041 Propellant" (Confidential).

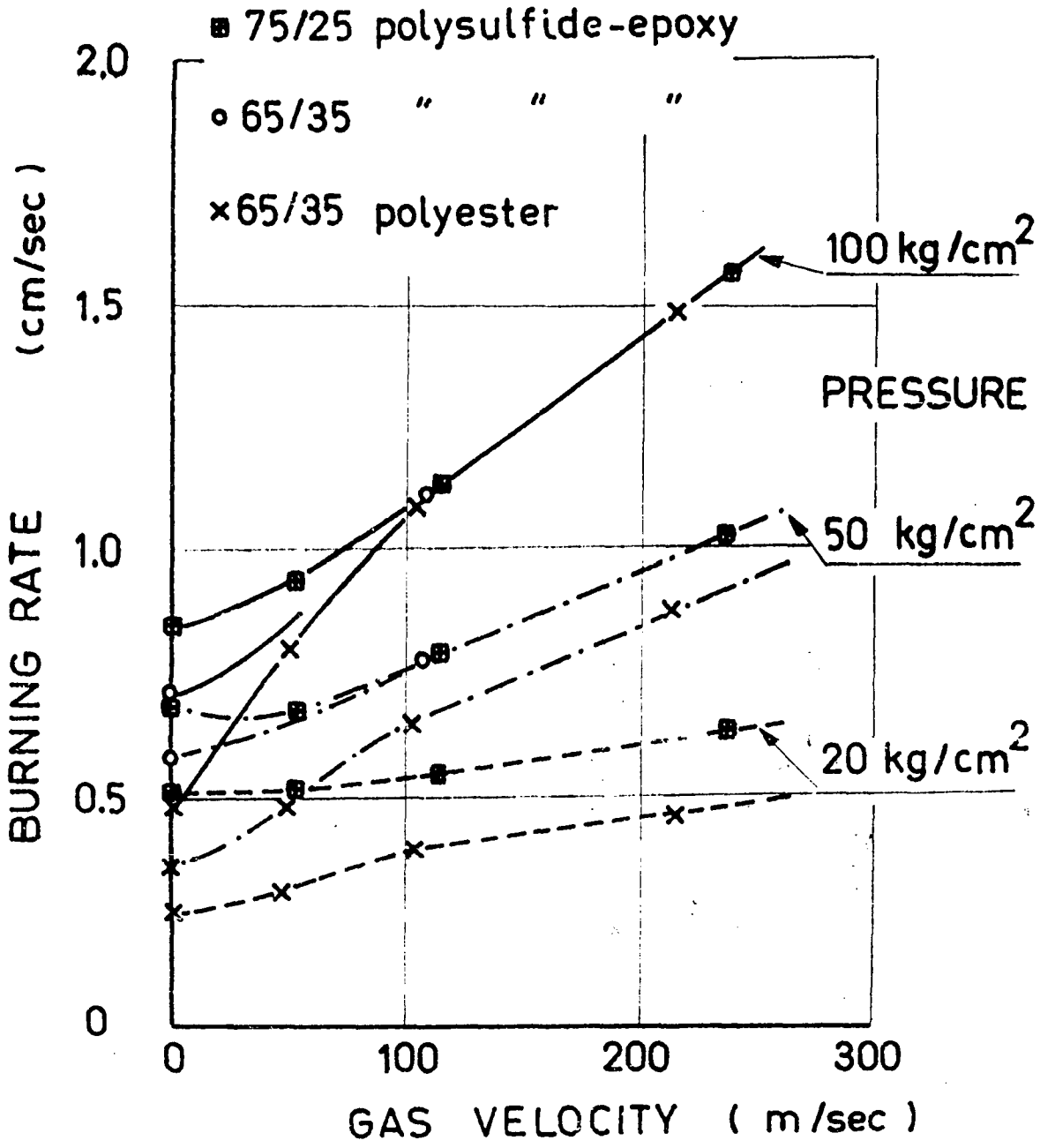

■ 75/25 polysulfide-epoxy
○ 65/35 " " "
× 65/35 polyester
100 kg/cm²
PRESSURE
50 kg/cm²
20 kg/cm²
BURNING RATE (cm/sec)
2.0
1.5
1.0
0.5
0
0
100
200
300
GAS VELOCITY (m/sec)

FIG.5

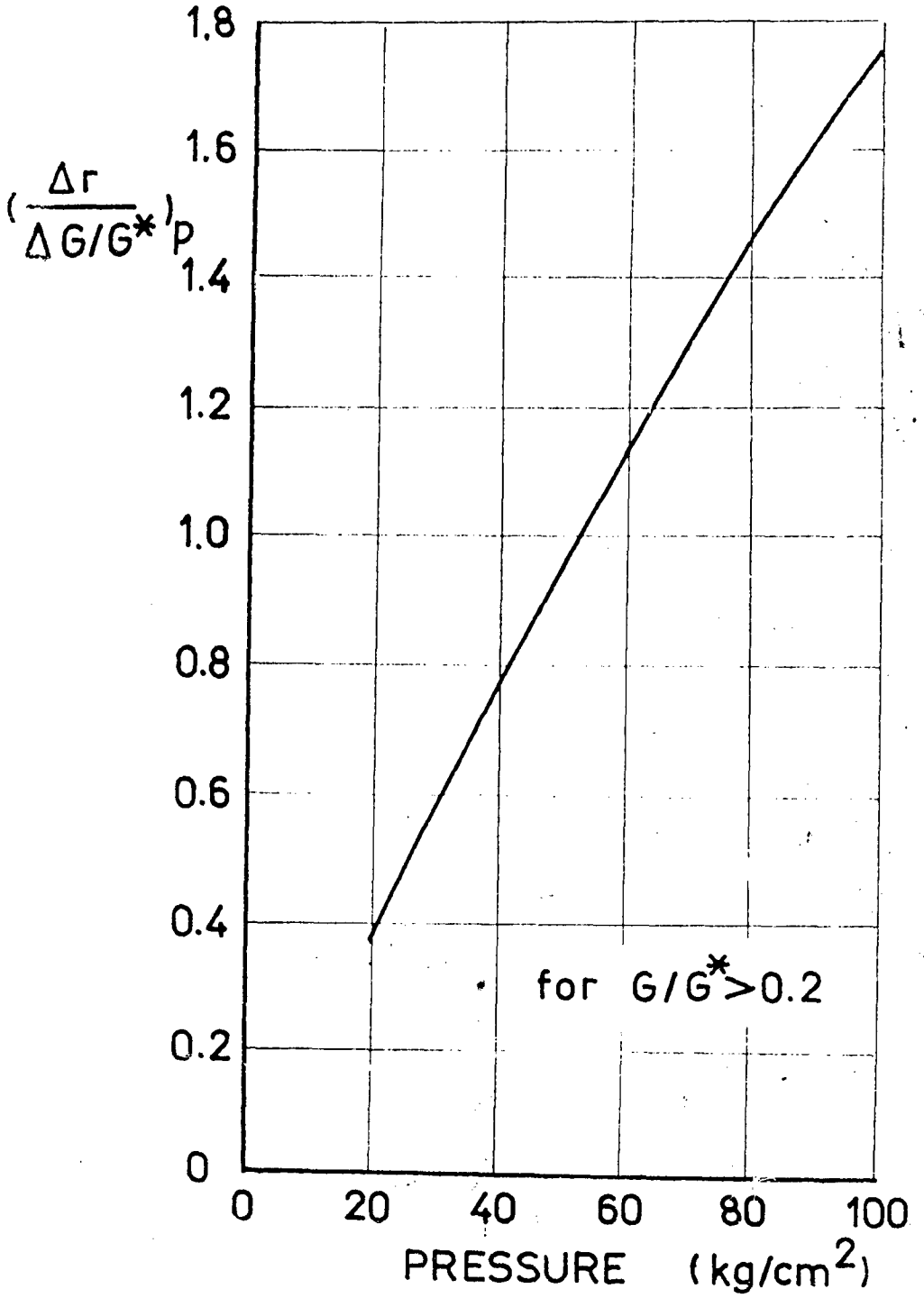

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
$(\frac{\Delta r}{\Delta G/G^*})_P$
for $G/G^* > 0.2$
0
20
40
60
80
100
PRESSURE (kg/cm^2)

FIG. 6

Using Green's relationship, these authors computed the values of k_M which permit to fit best the pressure-time traces obtained by firing the eight grains represented by figure 7. The results of this computation and the comparison with the data obtained by Green are represented on figure 8 from which it is seen that in most cases the erosive coefficients are significantly smaller than those measured by Green although in two cases they fall almost exactly on his average line.

These erosion coefficients k_M are also represented as a function of the configuration factor χ on figure 9 which suggests that erosive burning increases with grain complexity, the least squares line equation being:

$$k_M = 0.21\ \chi^{0.38}.$$

The eight tested grains were differing much in configuration factor χ, in port to throat area ratio H, and in standard burning rate $r_{o,std}$, at 70.3 kg/cm^2, as indicated by figure 7.

It is, however, most difficult to draw definite conclusions from these results since the mean chamber pressure and the port area (representing the scale) of these motors have not been reported. It is most probable that these two factors have a significant influence on k_M and under the assumption of similar chamber pressures figure 8 suggests that the experiments of Fenech and Billheimer have been performed with full scale motors of much larger dimensions than the small test rockets used by Green.

It must be emphasized, however, that the interpretation of these results is most delicate in terms of the erosion coefficient k_M defined by an empirical equation which does not take into account the possible existence of a velocity threshold. For instance, it is not surprizing that grain B of figure 7, whose port throat area ratio is equal to 10, is characterized by the lowest value of k_M. Indeed, under such conditions of rather low erosion, it is probably operating near the threshold velocity and Green's equation can hardly be expected to

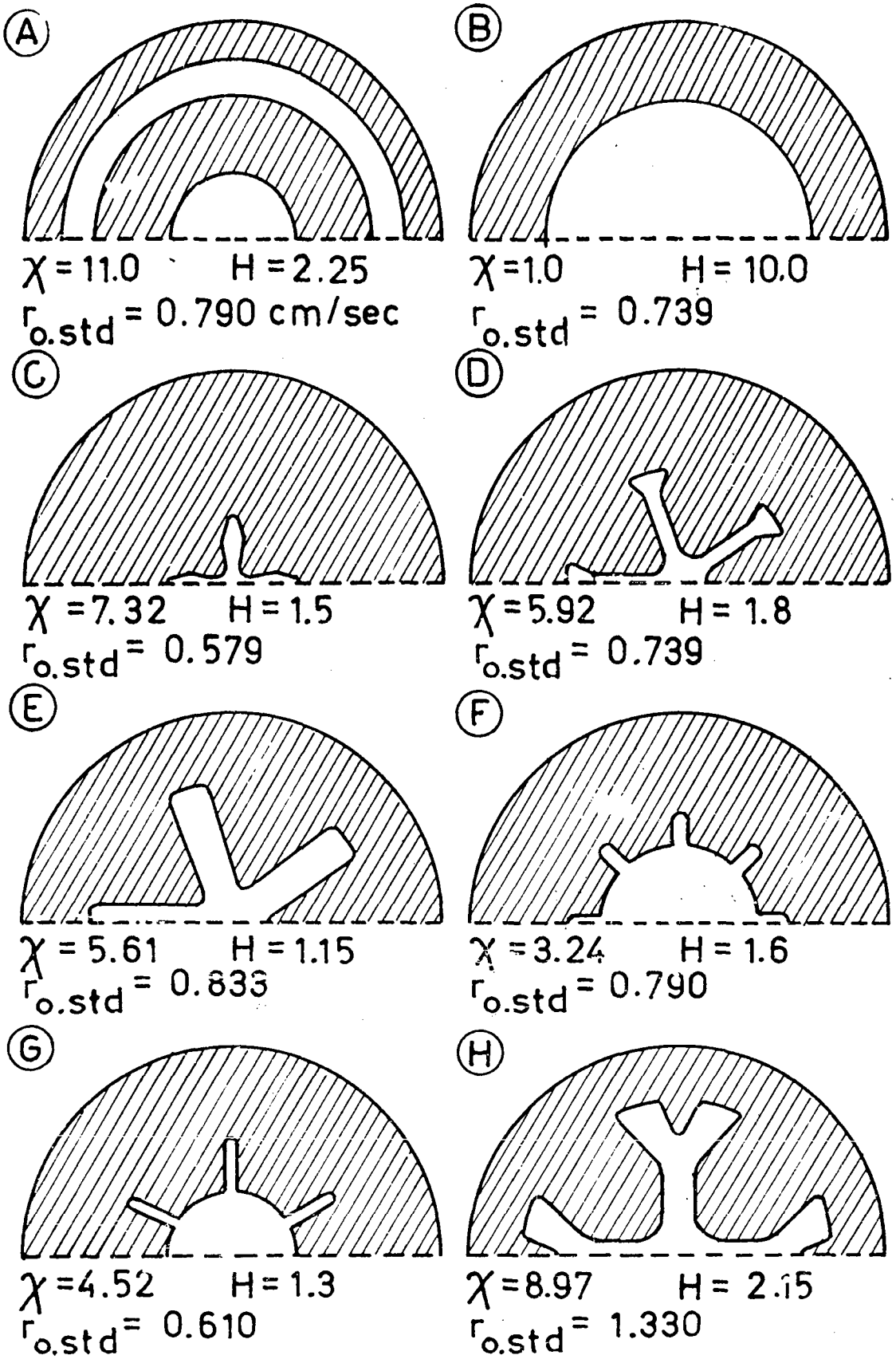

A
χ = 11.0 H = 2.25
r o.std = 0.790 cm/sec
B
χ = 1.0 H = 10.0
r o.std = 0.739
C
χ = 7.32 H = 1.5
r o.std = 0.579
D
χ = 5.92 H = 1.8
r o.std = 0.739
E
χ = 5.61 H = 1.15
r o.std = 0.833
F
χ = 3.24 H = 1.6
r o.std = 0.790
G
χ = 4.52 H = 1.3
r o.std = 0.610
H
χ = 8.97 H = 2.15
r o.std = 1.330

FIG. 7

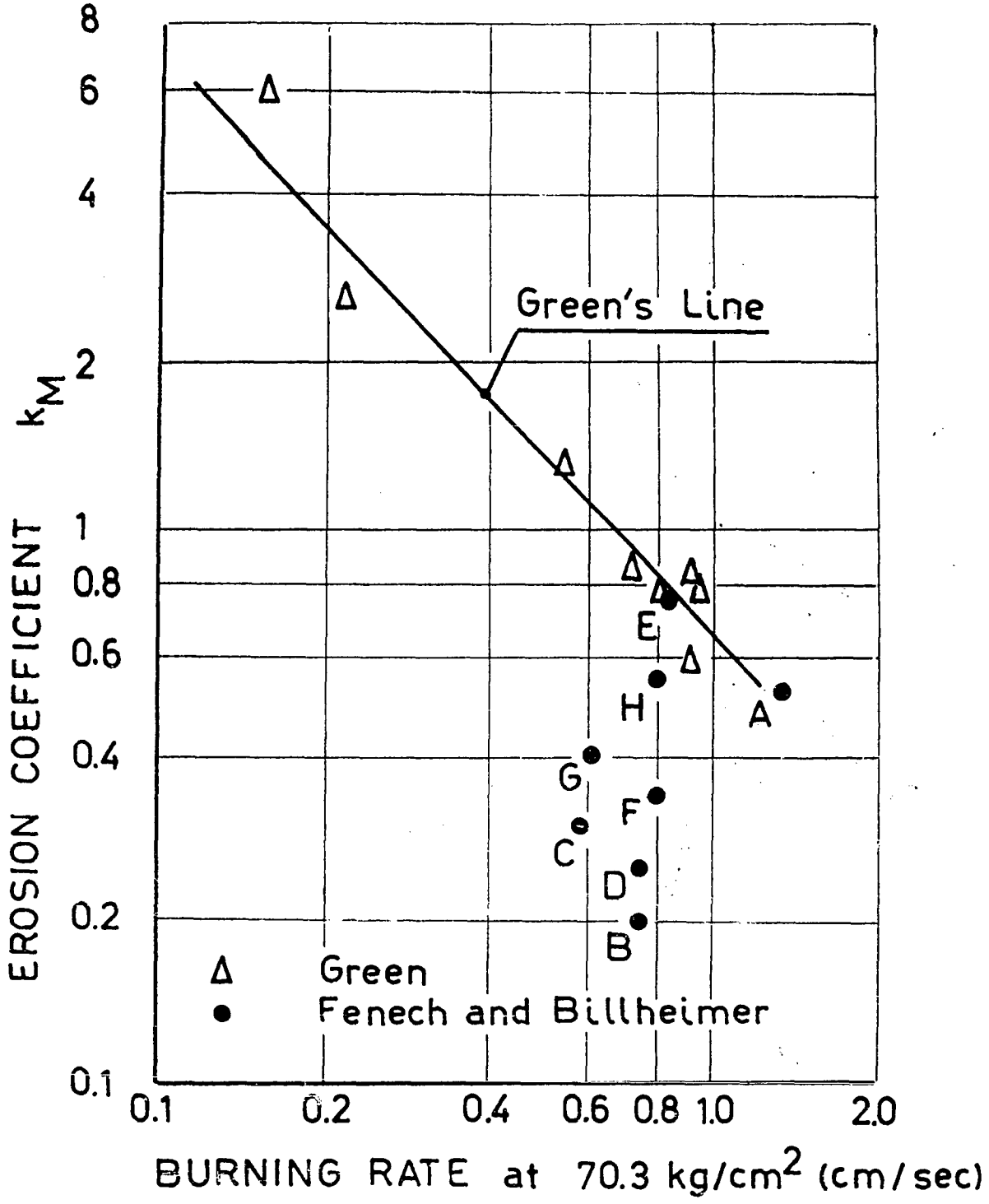

8
6
4
2
1
0.8
0.6
0.4
0.2
0.1
k_M
EROSION COEFFICIENT
Green's Line
A
B
C
D
E
F
G
H
Δ Green
● Fenech and Billheimer
0.1
0.2
0.4
0.6
0.8
1.0
2.0
BURNING RATE at 70.3 kg/cm^2 (cm/sec)

FIG. 8

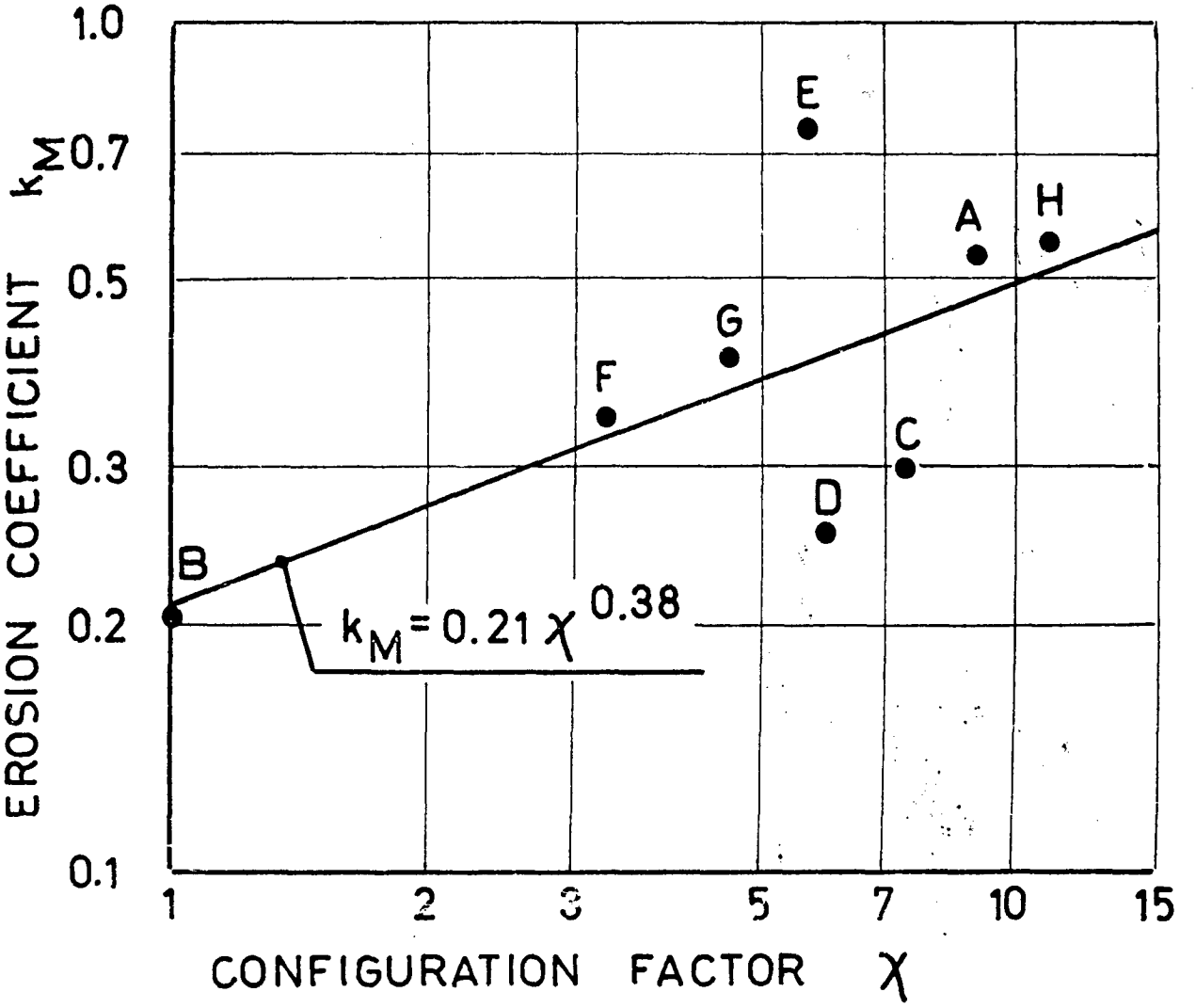

1.0
0.7
0.5
0.3
0.2
0.1
EROSION COEFFICIENT k_M
1
2
3
5
7
10
15
CONFIGURATION FACTOR χ
A
B
C
D
E
F
G
H
$k_M = 0.21\,\chi^{0.38}$

FIG.9

represent accurately the actual phenomenon.

The results obtained by Fenech and Billheimer are average values computed in the assumption of an equal burning rate along the perimeter of each cross-sectional area. In fact Dickinson, Jackson and Odgers reported higher burning rates on the tips of the arms of certain grain design, than on the rounded portions and sides of the arms [18]. These authors have shown that this difference in burning rates decreases when the grain design is such that the local ratio of burning perimeter to available port area for gases does not vary much from one point to another, in a cross-section. They attributed possibly the phenomenon to cross-flow. Another explanation can be found in the influence of local port scale which can be assumed to cover both the influence of motor scale (overall effect) and that of grain design (local effect).

A quantitative theory in this direction is given in section 5.

C. Experimental Techniques.

Without entering into the detailed description of the experimental techniques, it is essential to emphasize that measurements on erosive burning can be obtained by two ways.

In the first technique the burning rate measurement is made on the main grain, either by interrupting the combustion [12, 13] through suitable probes embedded in the propellant [18] or by analysis of the engine performance curve [17]. Figure 10 represents the experimental motor used by Green [13].

In the second technique, the test sample is separate from the main charge, and in general located in a relatively long pipe leading to the nozzle [14, 15]. In some cases, however, the nozzle itself, or part of it, is made of propellant [5, 6, 7, 14]. Figure 11 represents the different arrangements used by Lake and Marklund which have not reported a significant difference between the measurements made with

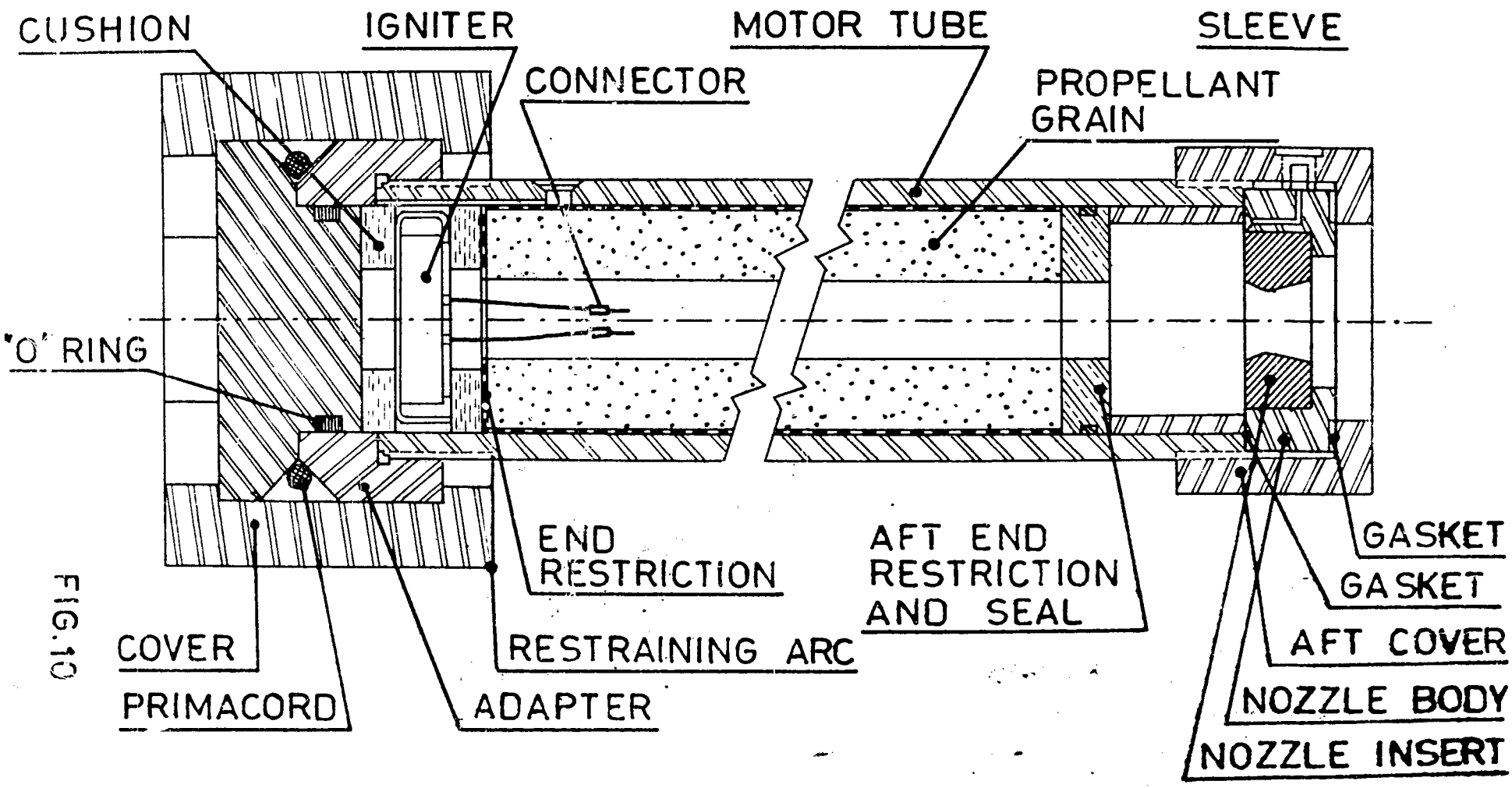

CUSHION
IGNITER
CONNECTOR
MOTOR TUBE
SLEEVE
PROPELLANT GRAIN
'O' RING
END RESTRICTION
AFT END RESTRICTION AND SEAL
GASKET
GASKET
AFT COVER
NOZZLE BODY
NOZZLE INSERT
COVER
PRIMACORD
ADAPTER
RESTRAINING ARC

FIG.10

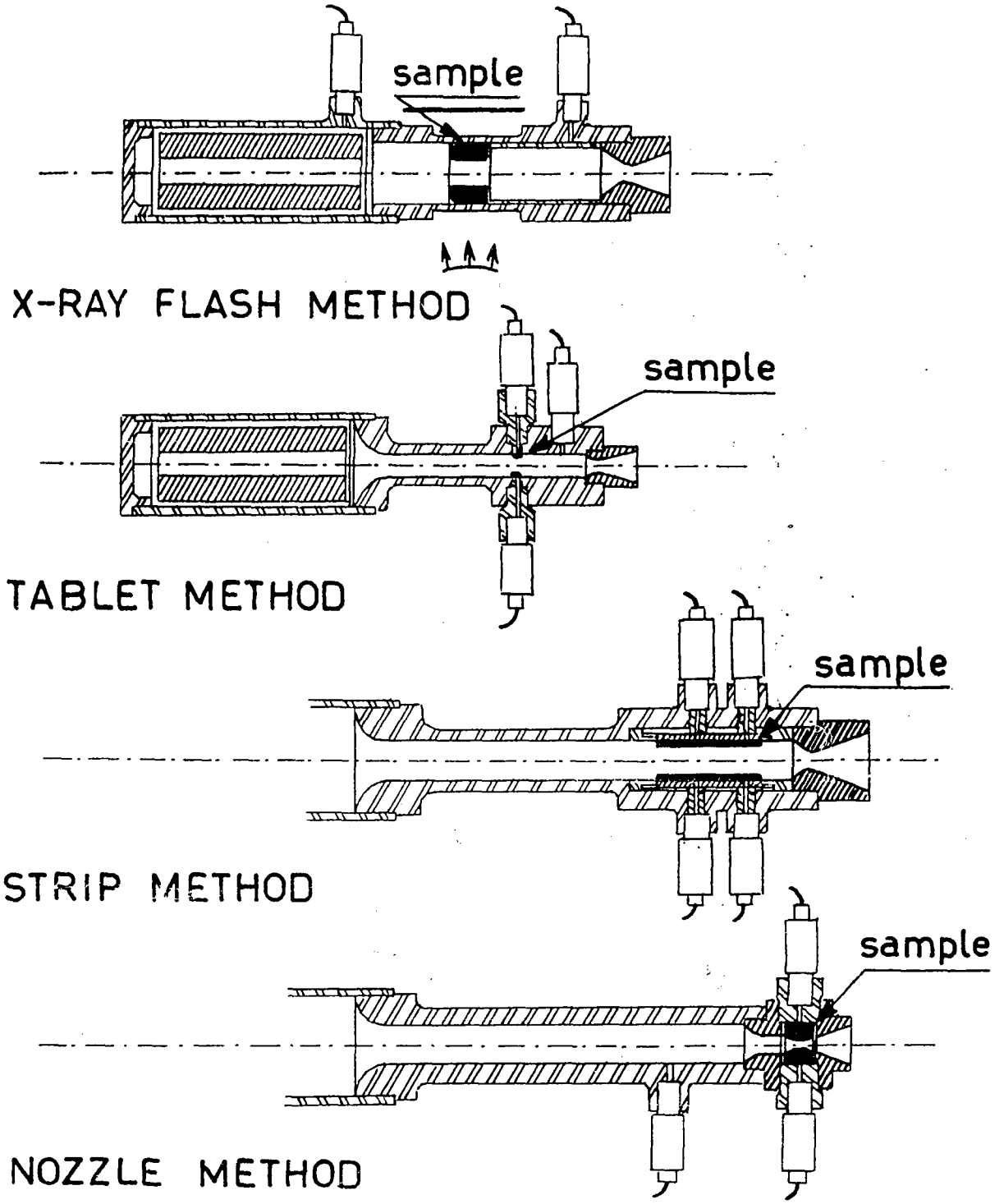

sample
X-RAY FLASH METHOD
sample
TABLET METHOD
sample
STRIP METHOD
sample
NOZZLE METHOD

FIG. 11

tablets and strips [14, 15] .

It is probable that the selected experimental technique somewhat influences the measurements. Indeed in the first method,as pointed out before, the length to diameter ratio of the perforation is seldom sufficiently large for neglecting the two-dimensional nature of the flow field which is influenced by the distance from the fore end of the grain and by mass-addition.

On the other hand, in the second method using a sufficiently long pipe, a fully developed turbulence can be assumed. Nevertheless the influence of the interaction between main flow and mass-addition due to the test sample can hardly be assessed.

In fact the flow fields obtained by the two methods are somewhat different and it is not surprizing that the results obtained by the second technique yield in many instances somewhat larger values of erosive burning than those measured on the main charge (see section 3 - B).

4. THEORETICAL STUDY OF EROSIVE BURNING OF AMMONIUM PERCHLORATE PROPELLANTS

A. Burning Mechanism of Ammonium Perchlorate Propellants.

Before proposing a model of erosive burning of ammonium perchlorate propellants, it is necessary to study in some details the burning mechanism of these propellants.

The problem is presently rather well understood, owing to the recent results obtained by professor M. Summerfield and his group at Princeton University [19] who have confirmed the theoretical predictions previously proposed by Jaumotte and Vandenkerckove [20] from which the following analysis is partially drawn.

Much information can be obtained simply by comparing the burning rate of propellants to that of pure ammonium perchlorate, as reported by Friedman and his coauthors [21, 22]. The burning rates of four propellants using polystyrene as fuel-binder and differing only by mixture ratio and granulation are taken from Summerfield and Marklund's works [14; 23]. The comparison given by figure 12, shows that the burning rate of the propellant can be higher or lower than that of pure oxidizer, depending on pressure, mixture ratio and granulation; it can be summarized as follows:

a - for coarse granulations and low oxidizer contents, the propellant burning rate is higher at low pressure and smaller at high pressure than that of pure perchlorate.

b - for fine granulations and high oxidizer contents, the burning rate is higher at all pressures in the considered range,

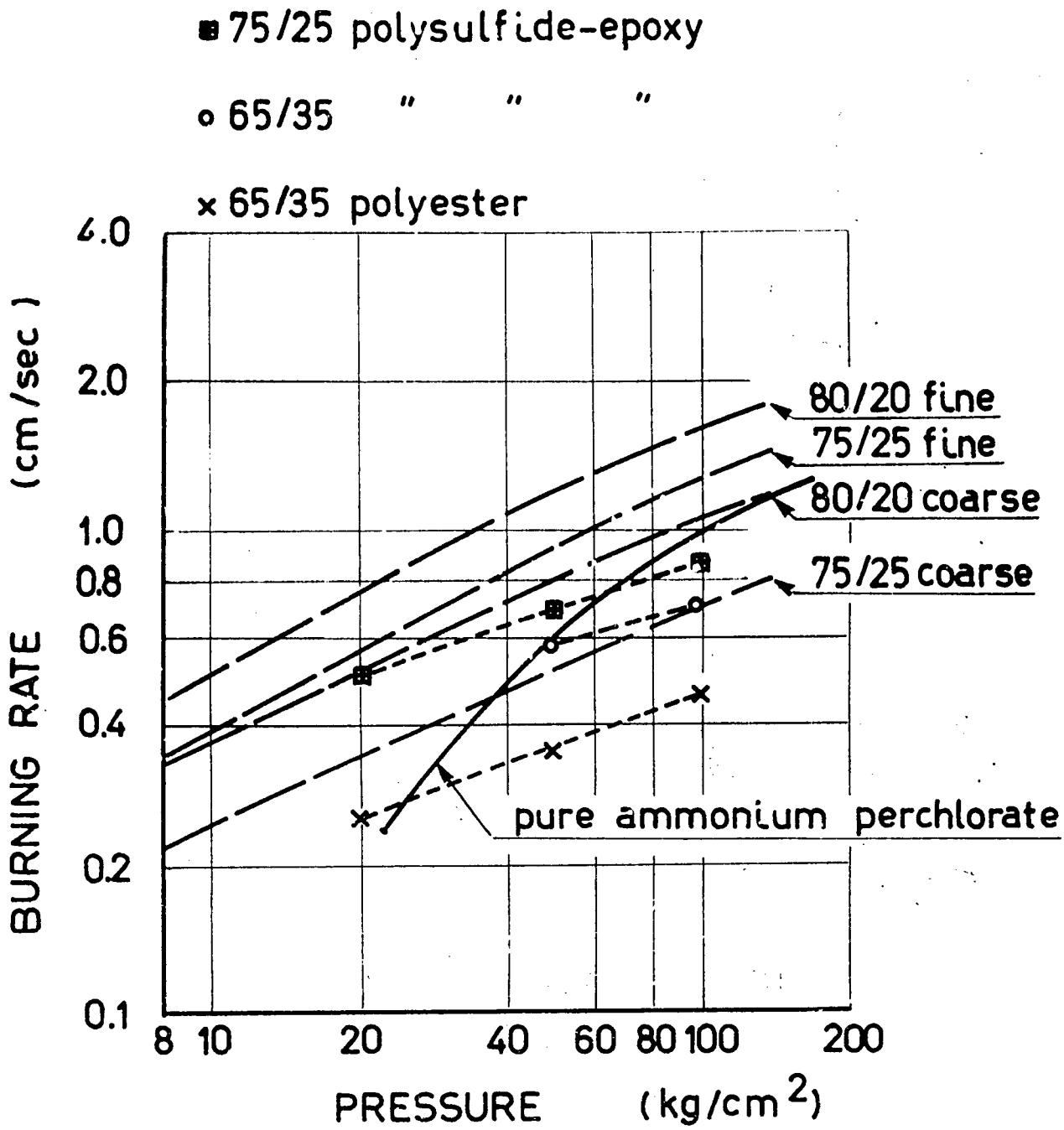

■ 75/25 polysulfide-epoxy
○ 65/35 " " "
× 65/35 polyester
4.0
2.0
1.0
0.8
0.6
0.4
0.2
0.1
BURNING RATE (cm/sec)
8 10 20 40 60 80 100 200
PRESSURE (kg/cm²)
80/20 fine
75/25 fine
80/20 coarse
75/25 coarse
pure ammonium perchlorate

FIG. 12

c- below approximately 50 kg/cm^2, the combustion index n of the propellant (as given by the classical law $r = ap^n$) is definitely smaller than that of pure perchlorate which, apparently, becomes higher than unity below 40 kg/cm^2.

d- For pure perchlorate, Friedman indicates a limit of flammability at about 22 kg/cm^2 while Summerfield has been able to measure steady propellant combustion down to one atmosphere. This fact suggests that the burning mechanisms are somewhat different in the low pressure range.

e- Finally the near constant combustion index n exhibited by most propellants in the full pressure range does not suggest that the phenomenon which controls the propellant burning rate, namely some kind of interaction between the oxidizer and the fuel, is basically different above and below the burning rate of pure perchlorate.

X X X X

It seems reasonable to assume that in the propellant a single oxidizer particle burns at least as fast as pure perchlorate at the same pressure. Indeed the decomposition zone of the oxidizer, being of the order of one micron or less, is generally much thinner than the particle dimensions and the effect of the interface can thus be neglected. The expression "at least as fast" has purposedly been used since the burning rate of pure perchlorate appears as a lower limit and heat can conceivably be brought from the main flame zone back to the oxidizer for increasing its temperature and deflagration rate.

It appears, therefore, that in the region situated below the deflagration curve of pure ammonium perchlorate, the burning rate of the oxidizer is faster than the average burning rate and that fuel peaks are most probably protruding the surface.

On the other hand, above the deflagration curve of pure ammonium perchlorate, no clear conclusions can be drawn at this point since the lower limit of the oxidizer deflagration rate in the propellant is only known.

If the decomposition flame is the only process of importance, the perchlorate particles will protrude above the surface of the faster pyrolyzing fuel; if significant heat transfer exists between the diffusion flame and the surface, however, both situations can prevail and we must rely on experiments.

In fact, early experiments have shown that above the deflagration curve of the pure oxidizer, at atmospheric pressure, large ammonium perchlorate crystals are protruding from the main surface [3, 23].

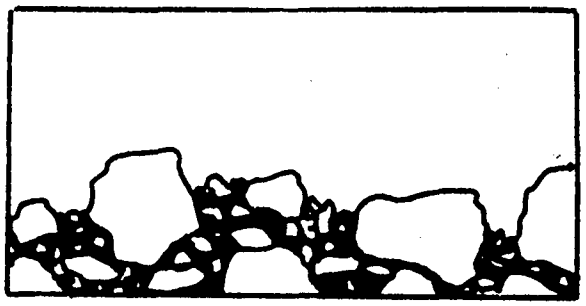
Later experiments provided much more precise information. Using high speed cinematography, Barrère observed a decrease in oxidizer particle protrusion with increasing pressure [24]. The interpretation of these excellent cinematographic records, for determining the surface structure, remains delicate, especially in the high pressure range.

After similar attempts, Summerfield's group, therefore, developed a method whereby small pieces of burning propellant can be extinguished suddenly by rapid evacuation of the burning vessel due to burst of a rupture disk [18]. This method is believed to leave the propellant surface intact and unaffected by the rapid pressure drop, for microscopic study of the structure. The pictures taken by this method show that at low pressure the oxidizer crystals project above the fuel surface. As the pressure increases, the crystals become flush and eventually recede deeply into the fuel, as schematized by figure 13. Very finely ground oxidizer particles, however, may be thrown away from the surface as soon as they are reached by the flame.

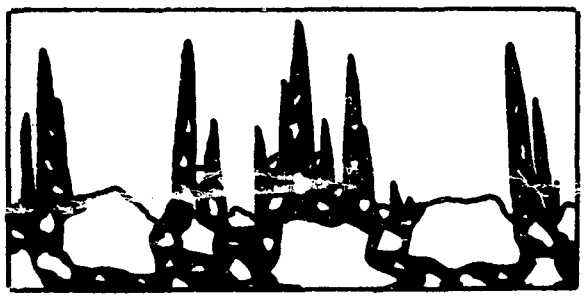
For our present purpose several conclusions can be drawn from these observations.

a - In the low pressure range, below 30 kg/cm^2 approximately, the burning rate of the propellant is much higher than that of the oxidizer, and most probably some heat must be transferred from the main reactions between oxidizer and fuel vapors, back to the surface.

b - It seems doubtful, however, that this heat transfer is homogeneous all over the surface.



LOW PRESSURE



HIGH PRESSURE

FIG. 13

Indeed, at the considered pressure, according to Summerfield, the characteristic chemical time of the reaction between oxidizer and fuel vapors is much shorter or at least of the same order of magnitude than the characteristic diffusion time [18]. Highly exothermic reactions, therefore, most probably take place very close to the surface at the interface of the oxidizing and reducing streams. In this region, only a small fraction of the gas is involved but this may be sufficient for modifying the surface temperature locally at the interface which has its own regression rate.

It appears therefore, that the regression rate of the interface between oxidizer and fuel is of particular importance in controlling the burning rate of the propellant, in the low pressure range. This conclusion is consistent with the effect of fuel nature, and, overall, of mixture ratio and granulation. Indeed a larger oxidizer percentage and a finer granulation both increase the length of the rate controlling interface and the number of crystals reached per unit time, thus reducing the distance actually travelled by the interface regression per unit length burned perpendicular to the average surface.

c - It must be emphasized, however, that in the whole pressure range the regression rates of the fuel, oxidizer and interface are not much different. In particular in the low pressure range the interface to oxidizer regression rate ratio cannot be much higher than 1.57 unless ammonium perchlorate particles are rooted up as represented very schematically by figure 14 drawn in the oversimplified assumption that the regression of a spherical particle is unaffected by the interface.

In fact the actual phenomenon is almost certainly much more complex; the interface regression rate may be influenced by other factors such as particle size and time, but the general conclusion of similar regression rates still remains valid.

d - In the high pressure range, above approximately 60 kg/cm^2, the burning rate of all the propellants whose tests have been reported in the open litterature is never much higher than the regression rate of the oxidizer, at least in the absence of ballistic modifiers. It can, however, be much lower but it is in fact often rather similar [23].

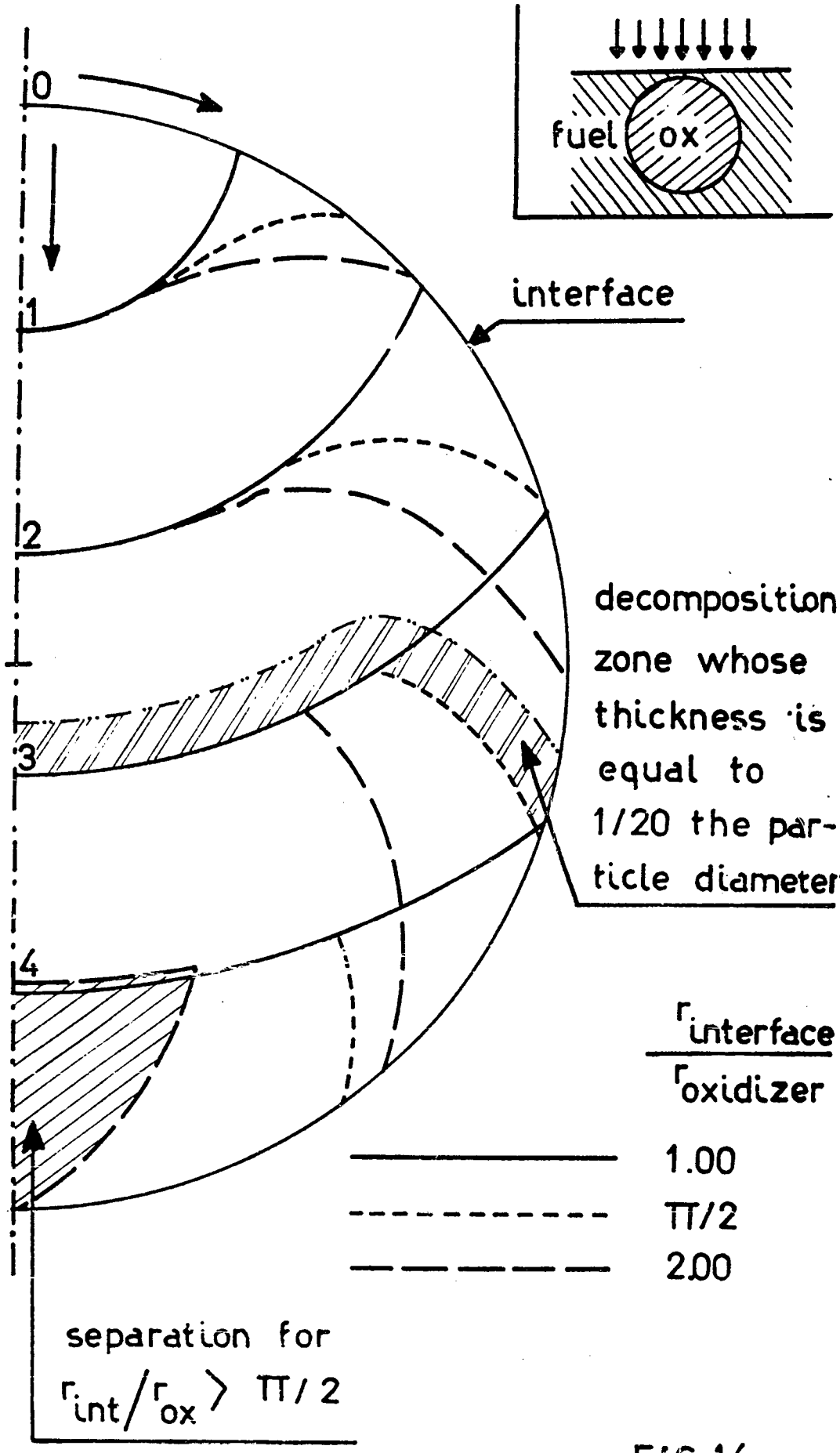

0
1
2
3
4
fuel
ox
interface
decomposition zone whose thickness is equal to 1/20 the particle diameter
$r_{interface}$ / $r_{oxidizer}$
1.00
π/2
2.00
separation for $r_{int}/r_{ox} > \pi/2$

FIG.14

This suggests that in the high pressure range the main diffusion flame does not play anymore a significant role in transfering heat towards the surface since otherwise the propellant burning rate would be consistently larger.

It is not our purpose to discuss much further the complex burning mechanism of ammonium perchlorate propellants; the preceding considerations, however, are necessary for studying erosive burning of such propellants.

B. Erosive Burning of Ammonium Perchlorate Propellants.

Our work relies heavily on the data obtained by Lake and Marklund, and represented on figure 5 [14]. These results exhibit a most interesting behaviour.

At high pressure (100 kg/cm^2) the burning rate without erosion of the three considered propellants depends in the normal way on mixture ratio and fuel nature, the main particle diameter remaining constant (24 - 30 μ) in the experiments.

Surprizingly enough, however, in the presence of a sufficiently strong erosion, above 100 m/sec, the influence of mixture ratio and fuel nature quickly disappears, and all three propellants exhibit an identical burning rate - versus - gas velocity relationship.

It appears therefore, that the burning rate without erosion can be viewed as an abnormal behavior and that in the presence of erosion, a classical burning law of the form :

$r = r_o$ multiplied by a function of erosion severity

is misleading since the reference rate r_o does not influence appreciably the burning rate-versus-velocity relationship.

On the other hand, at medium and low pressures (50 and 20 kg/cm^2) this behaviour does not hold true anymore.

In these experiments, indeed, the influence of fuel nature remains

in the presence of erosion, while the influence of mixture ratio still disappears at 50 kg/cm^2 and insufficient data leaves the question open at 20 kg/cm^2.

X X X X

In an attempt to explain these phenomena, the burning rates without erosion of the three propellants used by Marklund and Lake have also been plotted on figure 12. The correlation between figures 5 and 12 is interesting. At high pressure, when the strand burning rates of the low mixture ratio propellants tested in Sweden are below the deflagration curve of pure ammonium perchlorate, the influence of composition disappears with erosion while at medium and low pressures, when the burning rate of the faster composition is above, the influence of composition subsits, at least partially. The fact that at 50 kg/cm^2 the influence of fuel nature subsists in the presence of erosion while the influence of mixture ratio still disappears suggests that a distinction must be made between the effects of fuel nature and mixture ratio on burning mechanism.

X X X X

Furthermore one can expect that the controlling factor of these phenomena is not the relative magnitude of the propellant and oxidizer regression rates, but rather the surface structure.

Taking for granted that erosive burning results primarily from the increasing heat transfer which takes place just above the surface, due to the flow, the following physical model can be proposed. With the high rugosity characterising the burning surface one can hardly assume the existence of a normal laminar sublayer above the surface protrusions, but it is reasonable to assume that these peaks are eroded much more severely than the rest of the surface which then becomes smoother and smoother with increasing erosion.

a - At low pressure when these protrusions consist in oxidizer particles, their erosion does not influence appreciably the burning rate until the surface becomes sufficiently flat and an apparent "threshold velocity" exists below which no significant erosion takes place.

In the presence of a strong erosion the fuel nature still influences the burning rate, a phenomenon which confirms the conclusion that the regression of the oxidizer particles is markedly accelerated by heat transfer from at least part of the diffusion flame.

b - At medium pressure some fuel peaks have probably appeared, the threshold velocity has almost disappeared except for the higher mixture ratios but the fuel nature still influences somewhat the burning rate under severe erosion conditions.

c - At high pressure, the fuel peaks which protrude from the surface are first eroded. Due to the high oxidizer content their erosion results in new oxidizer crystals being reached by the flame sooner than without erosion.

In this case, no threshold velocity exists and figure 5 shows that the steepest increase in burning rate with gas velocity corresponds to the largest difference between erosionless burning rate and deflagration rate of pure perchlorate (largest fuel protrusions).

Furthermore it has been concluded previously that at high pressure no significant heat from the main diffusion flame reaches the oxidizer particles. These conclusions are confirmed by the experimental fact that the influence of fuel nature, mixture ratio and probably granulation disappears when erosion becomes sufficiently severe, thus indicating that the decomposition of the oxidizer crystals becomes the single controling factor of the burning rate, the surface being assumed to be sufficiently smooth (without erosion the burning rate is also controlled to some extent by granulation and mixture ratio, a fact which could perhaps be explained by the probability, for the flame to pass from one exidizer crystal to another).

When the surface is flattened by erosion, the oxydizer, fuel and interface regression rates become equal. At high pressure the problem can, therefore, be treated as if the propellant is replaced by pure ammonium perchlorate (possibly catalyzed by suitable ballistic modifiers).

X X X X

For checking the validity of this physical model, it is possible to compute the slope of the experimental k_M - versus - r_o curve obtained by Green (see figure 4 taken from [13]) which proposed to represent erosive burning by the empirical expression :

$$r = r_o \ (1 + k_M \ G/G^*)$$

r_o being the burning rate without erosion, k_M the erosive coefficient and G/G^* the ratio of actual mass velocity ρV to its critical value[1].

The following computation is carried out at the reference pressure of 70 kg/cm^2 (about 1.000 psi) which can still be considered as a relatively high pressure.

At that particular pressure, interpolation of the data obtained by Lake and Marklund can be represented approximately by a straight line r - versus - G/G^* when r_o is equal to 0.65 cm/sec, and r = 1.97 cm/sec for $G/G^* = 1$, as schematized on figure 15. (see reference [1] and its figure 7 for complete treatment of this problem of internal ballistics, taking into account that :

$$\left(G^* \frac{\sqrt{R\,T_1}}{p_1} \right)_{A_r} = \sqrt{\frac{\gamma}{2(\gamma + 1)}} = 0.529 \text{ for } \gamma = 1.24.)$$

The empirical equation, therefore, gives:

$$k_M = \frac{1.97}{0.65} - 1 = 2.035$$

This value is much higher than the one measured by Green, for that particular burning rate, i.e.

$$k_M = 0.98$$

and the two series of experiments can only be correlated through the use of a rather large coefficient :

$$2.035 \ / \ 0.98 = 2.080$$

It is believed that this discrepancy can be explained as follows :

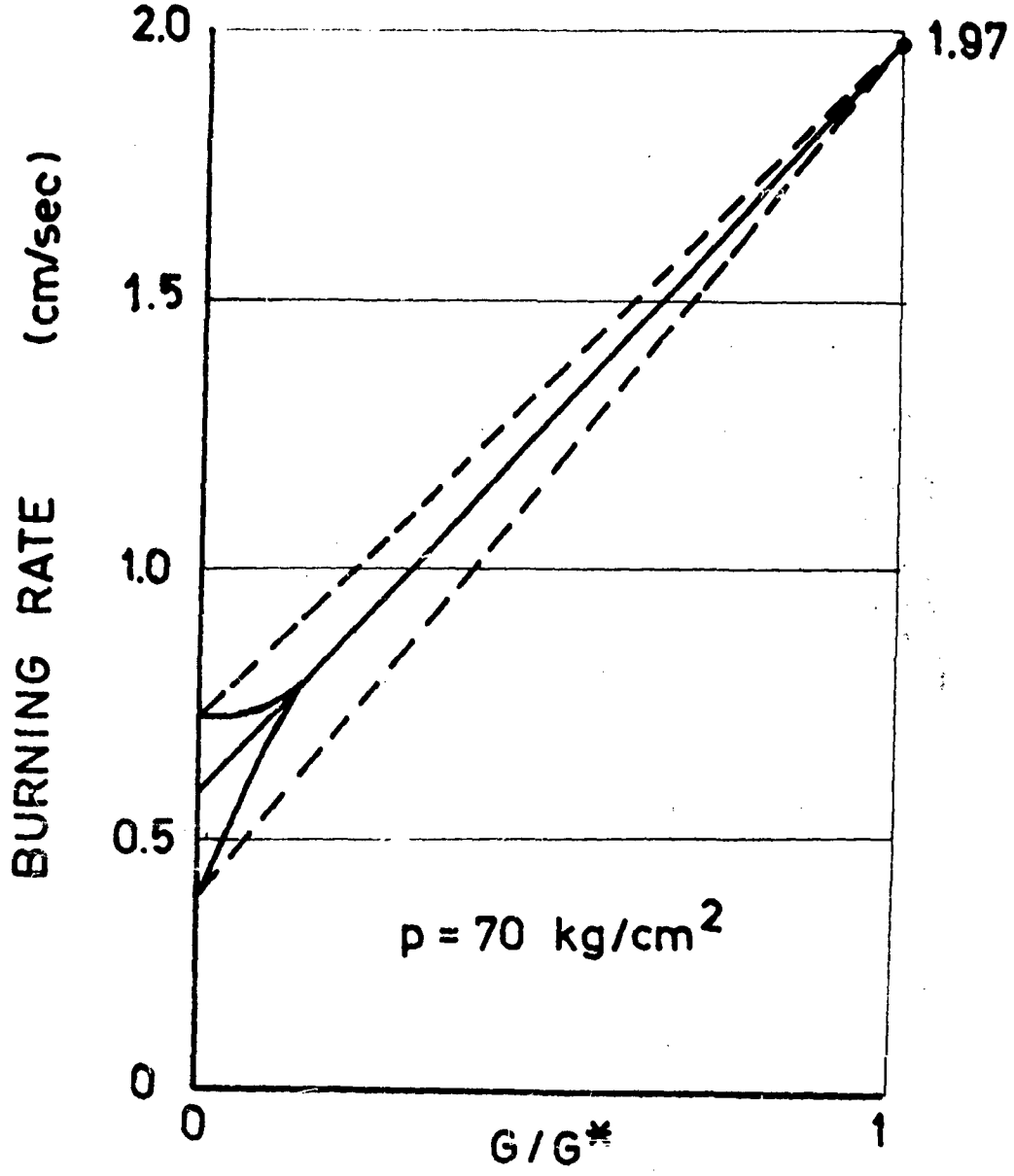


FIG. 15

1/ The experimental techniques are different as emphasized in section 3.

2/ Although Green correlated his results by using the reference burning rates at 70 kg/cm^2, his measurements have actually been made at a much smaller pressure, at least at the beginning of the burning time when erosive burning is the largest (a strongly progressive grain design was used.).

Under these conditions, an appreciably smaller erosive coefficient is consistent with the data obtained by Lake and Marklund.

In addition to a correlation coefficient equal to 2.080, if it is assumed that Green's measurements have been obtained near $G/G^* = 1$, the slope of the k_M - versus - r_o curve can be easily computed in the neighbourhood of the chosen point of reference ($r_o = 0.65$ cm/sec , $k_M = 0.98$).

Indeed the physical model predicts that under a severe erosion, the burning rate is independent of r_o and equal to 1.97 cm/sec in the case under consideration.

The empirical equation, therefore, gives for $_o = 1$ cm/sec :

$$1.97 = 1 \; (1 + 1.080 \; k_M)$$

or $$k_M = 0.466$$

Similarly, for $r_o = 0.5$ and 0.2 cm/sec, one gets respectively $k_M = 1.415$ and 4.250.

These results are compared with Green's data on figure 16. The correlation is fairly good, especially if the dispersion of the experimental points is taken into account.

Actually Green's data have been obtained for

$$G/G^* < 1$$

and a slightly higher correlation coefficient would have to be used (2.12 for G/G^*) resulting in a somewhat larger slope of the computed curve.

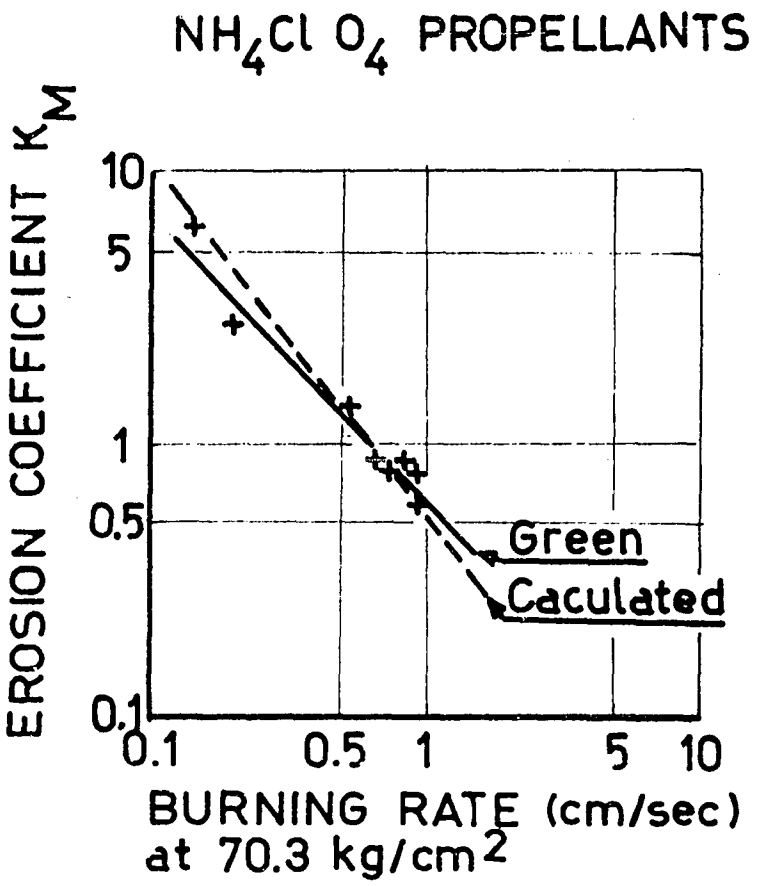

NH4Cl O4 PROPELLANTS
EROSION COEFFICIENT KM
10
5
1
0.5
0.1
0.1
0.5
1
5
10
Green
Caculated
BURNING RATE (cm/sec)
at 70.3 kg/cm2

FIG. 16

It must be emphasized, however, that the equation which defines k_M is only an approximate and empirical expression which barely represents the actual phenomenon in the low velocity range (see the difference between the plain and dotted lines on figure 15) and that it is, consequently, difficult to carry the comparison beyond this point.

Furthermore it must be kept in mind that Green's measurements were taken at relatively moderate pressure, in a range in which the fuel nature and possibly other factors are still of some importance under severe erosion.

In view of the drastic assumptions made, the preceding correlation does not prove rigorously the validity of the proposed model; it is nevertheless encouraging.

C. Mathematical Model of Erosive Burning.

α Solid-Phase Decomposition.

The following method is similar to the one proposed in reference [9] for computing the erosive burning of double base propellants, the so-called fizz zone being replaced by the oxidizer decomposition zone at the end of which temperature T_1 is obtained. As emphasized previously this approach is valid only at relatively high pressure, above 50 kg/cm^2, in a region where no significant heat transfer from the main flame zone takes place towards the surface, thus permitting to compute temperature T_1 by assuming an adiabatic decomposition reaction.

Under severe erosion , therefore, the propellant can be represented by a flat surface of pure ammonium perchlorate and the solid-phase decomposition, which is considered by the majority of the authors as the rate controlling step of the combustion, is given in terms of the surface temperature T_s by the Arrhenius type relationship [3, 8, 25] :

$$r = B \exp (- E / R_o T_s) \qquad (1)$$

with r the burning rate

B the preexponential factor

E the activation energy

and R_o the universal gas constant (1.985 cal/g.mole. °K)

Certain authors, however, use a slightly different expression [26, 27] :

$$r = B' T_s^{\beta} \exp (- E / R_o T_s) \qquad (1')$$

which in practice gives similar results.

β Heat Transfer across the Decomposition Zone.

It is assumed, hereunder, that the heat transfer across the gas-phase decomposition zone is due primarily to gas conductivity whereas the influence of turbulence and radiation can be neglected to a first approximation.

At a distance y_1 away from the burning surface, the chemical reactions characterizing the decomposition zone are completed, and in the absence of any heat transfer from the flame zone temperature T_1 is obtained.

In order to obtain, as a function of y, the temperature profile within the decomposition zone, the degree of completion of the reaction at each distance y from the surface is needed. This could be done through chemical kinetics considerations along the lines used by NACHBAR and others [25]. This, however, would increase very much the complexity of the problem and, overall, introduce many parameters whose numerical values are not accurately known, thus decreasing the confidence level in the results.

In accordance with several authors (Rice and Ginell, Parr and Crawford, Geckler), therefore, it is assumed, hereunder, that to a first approximation the total heat release takes place at once at the end of the decomposition zone, in the plane $y = y_1$ [8].

In relative motion, the oxidizer being fixed at the burning surface, no heat source is therefore encountered for

$$0 < y < y_1$$

and in steady state the conduction equation can be written:

$$k \frac{dt}{dy} = \rho_p r \quad c_p \left(T - T'_s \right) \qquad (2)$$

with k the thermal conductivity,

ρ_p the propellant specific mass,

$\rho_p r$ the flow rate per unit area of the surface,

and c_p the specific heat at constant pressure.

This realtionship expresses the equality of the heat flux by conduction towards the surface and of the heat flux leaving the surface in the form of enthalpy. The term $c_p T'_s$ represents the energy level of reference whose expression is established below.

By introducing mean values of the specific heat $\overline{c_p}$ and thermal conductivity $\overline{k}$, the preceding equation can be readily integrated between the burning surface ($y = 0$, $T = T_s$) and the end of the decomposition zone ($y = y_1$, $T = T_1$). It yields :

$$\frac{T_s - T'_s}{T_1 - T'_s} = \exp\left[- \rho_p \, r \, \frac{\overline{c_p}}{\overline{k}} \, y_1 \right] \qquad (3)$$

X X X X

The value of the energy level of reference $\overline{c_p}\, T'_s$ can be computed as follows: on the burning surface, for $y = 0$, a gaseous phase is produced at temperature T_s, and the passage, at that particular temperature, from solid to gas, can be represented by a reaction of the form:

$$\sum_1^n n_i \, S_i \rightarrow \sum_1^m m_j \, G_j \qquad (4)$$

S_i and G_j representing respectively the solid and gaseous species; n_i and m_j the corresponding numbers of moles. The quantity of heat $Q_s^{T_s}$ involved in this generally endothermic process is :

$$Q_s^{T_s} = \sum_1^m m_j \left(\Delta H_f^{T_s} \right)_{G_j} - \sum_1^n n_i \left(\Delta H_f^{T_s} \right)_{S_i} \qquad (5)$$

$\left(\Delta H_f^{T_s} \right)$ representing the heat of formation, at temperature T_s, of the considered species.

The term $\overline{c_p}\, T'_s$ has been introduced as the energy level of reference per unit mass. The heat reaching the burning surface serves for heating the solid propellant from its initial temperature T_i up to T_s and then

for achieving the phase change, a process which is generally accompanied by some chemical reactions, as indicated by equation (4). The energy balance per unit mass can, thus, be written :

$$\overline{C_s} \; (T_s - T_i) + Q_s^{T_s} = \overline{c_p} \; (T_s - T'_s) \qquad (6)$$

$\overline{C_s}$ being the mean specific heat of the solid phase and the specific heat c_p being assumed to remain constant in the decomposition zone.

The heat of formation is not readily tabulated at temperature T_s but rather at the standard temperature T_o = 25 °C, yielding :

$$Q_s^{T_s} = Q_s^o - \overline{C_s} \; (T_s - T_o) + \overline{c_p} \; (T_s - T_o) \qquad (7)$$

Combining equations (6) and (7) gives :

$$\overline{c_p} \; (T_o - T'_s) = Q_s^o + \overline{C_s} \; (T_o - T_i) \qquad (8)$$

from which the value of T'_s can be obtained.

The term $(T_o - T'_s)$ represents the fictitious temperature drop which would be necessary for vaporizing adiabatically the solid, assuming a constant mean value of the specific heat at constant pressure.

For an endothermic surface reaction , this term is positive and it is thus normal, although somewhat surprizing, that T'_s can take large negative values since it is not an actual temperature but rather represents a quantity of heat with its sign.

x x x x x

In the presence of erosion due to a flow parallel to the propellant surface, turbulence takes place in the combustion layer, increasing the temperature level and decreasing the thickness of the decomposition zone. The surface temperature, therefore, increases together with burning rate, and equation (1') can be written:

$$\frac{r}{r_o} = \left(\frac{T_s}{T_{so}}\right)^{\beta} \exp \frac{E}{R_o} \left(\frac{1}{T_{so}} - \frac{1}{T_s} \right) \qquad (9)$$

subscript $_o$ indicating the absence of erosion.

Within the decomposition zone, temperature T_1 is obtained at a point:

$$y_1' < y ,$$

where the decomposition reactions are possibly not yet entirely completed. The conduction equation can be written directly between that point y_1' and the burning surface, across a region in which the flow can be assumed to remain laminar.

Equations 3 and 9 give :

$$\frac{T_s - T_s'}{T_1 - T_s'} = \exp \left[- \rho_p \frac{\overline{c_p}}{k} y_1' r_o \left(\frac{T_s}{T_{so}} \right)^{\beta} \exp \frac{E}{R_o} \left(\frac{1}{T_{so}} - \frac{1}{T_s} \right) \right] \qquad (10)$$

Equations (9) and (10) permit to compute T_s and r/r_o corresponding to each value of the effective decomposition zone thickness :

$$y_1' < y_1$$

y - Fluid Dynamics.

The dependence of erosive burning on the effective decomposition zone thickness y_1', at the end of which temperature T_1 is obtained, must be supplemented by a relationship between y_1' and the mean flow velocity V (or Mach number, or mass velocity) parallel to the propellant surface.

Within the flame, the picture of separate zones is probably fairly good when it is applied to the case of an end-burning strand where the gas flow is approximately laminar (some turbulence, however, appears to take place at the interface between fuel and oxidizer vapors) and one-dimensional, directed normally away from the surface.

In the much more complex case of a significant velocity parallel to the surface, one can raise the question of the validity of this model.

It has been assumed, hereunder, that the presence of a strong velocity gradient in the boundary layer does not alter appreciably this picture in the laminar sublayer where all transport of heat and chemical species is accomplished by movements on a molecular scale.

In the turbulent region, however, eddies play an important role in the transport phenomenon and it is clear that the picture of separate zones does not hold anymore. Nevertheless one can expect that this flame structure still holds in the transition sublayer where turbulence is not yet fully developed and where the dimensions of the eddies are much smaller than the thickness of a zone.

Furthermore one can expect, as a working assumption, that inside the decomposition zone temperature T_1 is obtained exactly at the limit of the laminar sublayer. Indeed turbulence in the upper layers of the flame is not yet fully developed, its influence is not only to increase the thermal conductivity by transporting hot gases towards the surface but hitherto unreacted products are also transported back in the process in such a manner that they will react closer to the surface.

X X X X

The problem of predicting the boundary layer behaviour in a rocket motor perforation is a very complex one which does not appear to be rigorously tractable.

The effect of mass addition alone is already difficult to predict: for a plate, indeed, it results in an increased thickness of the laminar sublayer while for a pipe it may actually decrease the laminar sublayer since

the effect of fluid injection at the wall is to accelerate the main stream velocity [28]. The presence of severe temperature gradients in the flame , the complex grain design, and the fact that the length to diameter ratio of the perforation is in general relatively small still increase very much the complexity of the problem.

Nevertheless, in practical cases of erosive burning, the velocity component perpendicular to the surface does not, generally, exceed one per cent of the mean flow velocity, and it seems possible, following Corner and Geckler, to use the well know theory of flow in rough pipes. as a first approximation [4, 8] . Although this drastic simplification can hardly be completely justified on theoretical ground, it appears to give fairly good results in practice when the theory is used with caution and experimental data are exploited for computing the numerical value of some parameters in an effort to adapt the equation to the actual case under consideration.

X X X

In the theory of flow in rough pipes, the mean flow velocity V is expressed in terms of the so-called friction velocity v_x by the relationship:

$$V = v_x \left(1.75 + 5.75 \log_{10} \frac{Rv_x}{\nu}\right) \qquad (11)$$

where R is the pipe radius and $\nu = \mu/g\rho$ is the cinematic viscosity, μ being the absolute viscosity and $g\rho$ the specific weight.

In the laminar sublayer the flow pattern is entirely determined by the viscous stresses. Neglecting the velocity component perpendicular to the surface, therefore, it can be written, by analogy with the theory of pipes:

$$y^* = \frac{v_x y}{\nu} \qquad (12)$$

y^* being the so-called friction distance parameter and y the distance from the burning surface. Equation (12) defines the laminar sublayer up to a critical value of the friction parameter :

$$y^*_{cr}$$

which is characteristic of the problem and represents the distance at which turbulence appears. In the theory of rough pipes, the critical value is about 5; in the problem under consideration it is reasonable to expect a somewhat lower value due to the mass addition and the presence of the flame. In fact, in a previous computation dealing with a double base propellant [9], it has been found :

$$y^*_{cr} = 2.85$$

and in the following section, values ranging between 0.4 and 0.7 are found, depending on the ratio of perpendicular velocity to mean flow velocity, for ammonium perchlorate propellants whose flame is strongly heterogeneous (see figure 18).

According to the preceding assumptions, therefore, turbulence appears above plane y'_1 where temperature T_1 is reached in the absence of significant heat transfer from the main diffusion flame, and equation (12) can be written:

$$y^*_{cr} = \frac{v_x \, y'_1}{\nu} \qquad (13)$$

Equations (11) and (13) provide the relation between y'_1 and V, assuming that the proper value of y^*_{cr} is obtained from correlation of experimental data. Elimination of v_x between these two equations gives :

$$V = 5.75 \frac{y^*_{cr} \nu}{y'_1} \left[0.30435 + \log_{10} \frac{R \, y^*_{cr}}{y'_1} \right] \qquad (14)$$

8 - Numerical Application.

Under severe erosion the propellant can be schematized by a flat surface of pure ammonium perchlorate whose solid-phase decomposition is represented by equation (1) or (1'). Figure 17 represents the surface temperature T_s as a function of burning rate r, as given by the following three recent references :

A - Chaiken and Andersen [25] .

$r = 4600 \exp (- 20000/R_o T_s)$

B - Andersen and Chaiken [27] .

$r = 31\ T_s \exp (- 22000/R_o T_s)$

C - Johnson and Nachbar [26] .

$r = 5.88\ T_s \exp (- 19160/R_o T_s)$

r being given in cm/sec.

These empirical relationships have been obtained by "hot plate" pyrolysis. Figure 17 also represents a single point giving the lower limit of T_s as Friedman obtained by an entirely different technique consisting in the optical measurement of the surface temperature [21] .

X X X X

The strongly endothermic reactions occuring at the surface can be represented as follows [21, 26] :

$$NH_4Cl\ O_4\ (s) \rightarrow NH_3(g) + H\ Cl\ O_4(g) - 56.00 \text{ kcal/mole oxidizer} \qquad (4)$$

For the mean specific heat $\overline{c_p}$ in the decomposition zone, Johnson and Nachbar use [26]:

$\overline{c_p}$ = 38.08 cal/mole oxidizer, °K, in agreement with our computation, at 1300 °K, which gives $\overline{c_p}$ = 36.34 cal/mole oxidizer, °K.

For the present calculation, the following value has been selected:

$\overline{c_p}$ = 37.00 cal/mole oxidizer, °K.

Equation (8), therefore, can be written :

$$T_o - T'_s = \frac{Q^o_s}{\overline{c_p}} = \frac{56.000}{37} = 1514 \text{ °K}$$

for $T_i = T_o$ = 300 °K, and finally :

$$T'_s = - 1214 \text{ °K}.$$

It is clear that T'_s is not an actual temperature but rather represents an energy with its sign.

X X X X

The adiabatic combustion temperature of ammonium perchlorate is equal to temperature T_1 at the end of the decomposition zone. Our computation, assuming the simplified reaction:

$$NH_4\ Cl\ O_4\ (s) \rightarrow 1.5\ H_2O + H\ Cl + 0.5\ N_2 + 1.25\ O_2$$

gives :

$$T_1 = 1430\ \ ^\circ K$$

a value which is in agreement with :

$$T_1 = 1440\ ^\circ K$$

computed by Friedman [21] at 100 at. and taking into account the minor concentrations of Cl, NO and NO_2.

X X X

Friedman uses the following value of the thermal conductivity in the decomposition zone [21]:

$$k = 0.00016\ \ cal/cm\ sec\ ^\circ K$$

which gives :

$$\frac{\overline{c_p}}{\overline{k}} = 1937\ \ cm\ sec/g$$

Our computation, using Eucken's realtionship, gives at 1300 °K :

$$\frac{\overline{c_p}}{\overline{k}} = 1484\ \ cm\ sec/g$$

and

the following value has been selected for the present calculation:

$$\frac{\overline{c_p}}{\overline{k}} = 1750\ \ cm\ sec\ /\ g.$$

X X X

Using these numerical values, equation (10), describing the heat transfer across the decomposition zone, can be written:

$$\frac{T_s + 1214}{2644} = \exp\left(- r\ 3412.5\ y_1' \right) \qquad (10)$$

for $\rho_p = 1.95\ g/cm^3$.

Used together with equation (1) or (1'), it permits also to represent thickness y_1' as a function of r, for the three solid-phase decomposition laws which have been considered previously, as shown on figure 17.

It is seen that the curves representing both T_s and y_1', are relatively well grouped together : in the following computation, curves B have been rather arbitrarily selected.

X X X

Determination of the actual value of the critical friction distance parameter can be obtained through correlation of experimental data such as those of Lake and Marklund [14] which can be summarized as follows:

Propellant : 75/25 polysulfide - epoxy :

p $\frac{kg}{cm^2}$	$\bar{V}$ $\frac{m}{sec}$	r $\frac{cm}{sec}$	$\frac{V}{\bar{V}}$	T_s °K	y_1' 10^{-4} cm
100	150	1.257	0.00703	1124.0	0.297
	200	1.447	0.00607	1140.0	0.240
	250	1.619	0.00543	1153.6	0.200
50	150	0.865	0.00967	1082.2	0.485
	200	0.965	000809	1094.0	0.420
	250	1.053	0.00706	1103.5	0.373
20	150	0.568	0.01588	1036.0	0.850
	200	0.603	0.01264	1042.5	0.770
	250	0.636	0.01067	1048.0	0.720

where V is the velocity component perpendicular to the surface which, in the region of importance for T ≃ 1400 °K , is given by :

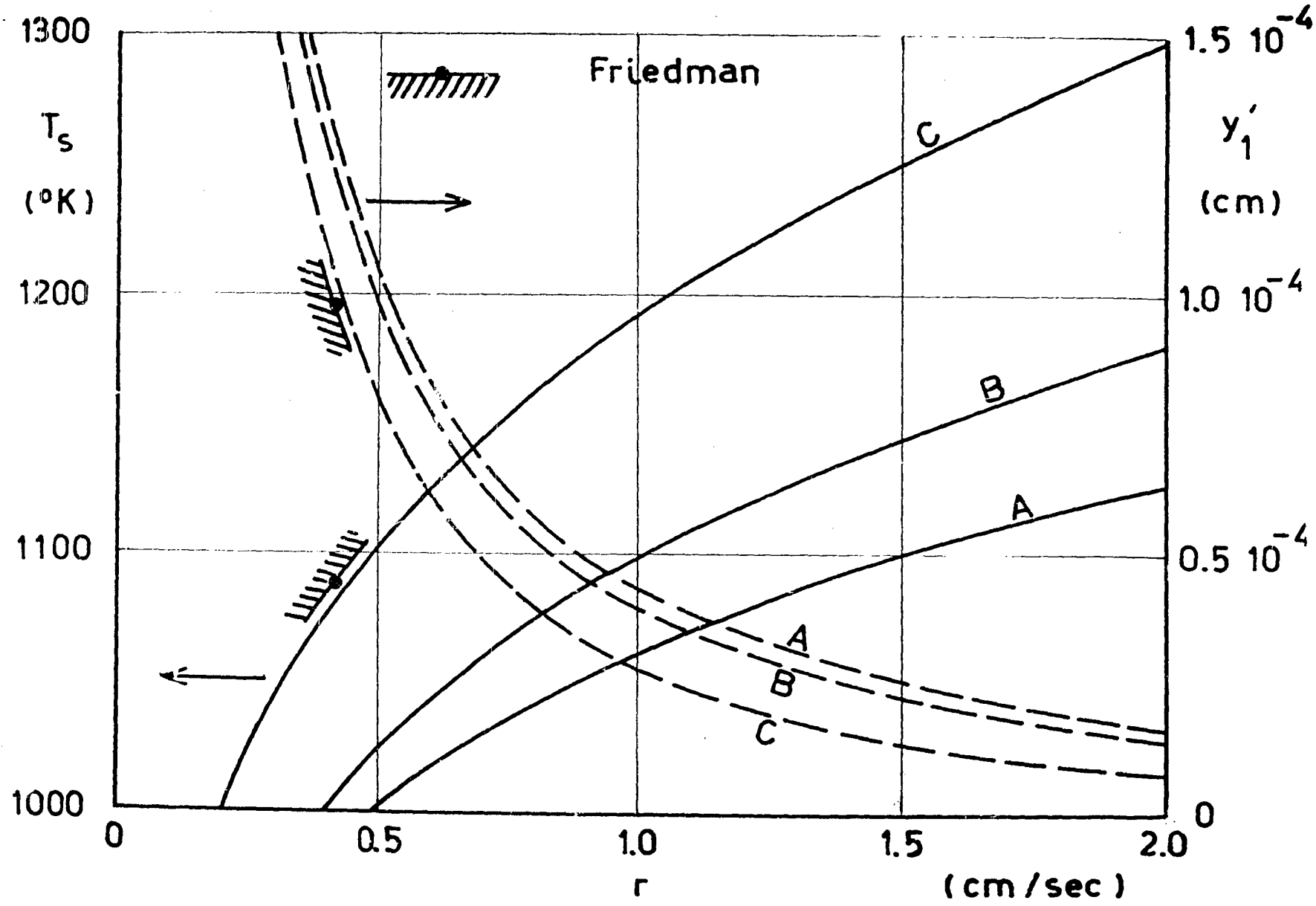

1300
1200
1100
1000
T_s
(°K)
Friedman
A
B
C
A
B
C
1.5 10^{-4}
1.0 10^{-4}
0.5 10^{-4}
0
y_1'
(cm)
0
0.5
1.0
1.5
2.0
r
(cm/sec)

FIG. 17

$$V_{\perp} = \frac{\rho_p}{\bar{\rho}}\, r = \frac{1.95\ r}{\dfrac{981 \quad 10^3 \quad p}{\dfrac{8136.6}{27} 10^4 \quad 1400}} = \frac{8400\ r}{p}$$

p being expressed in kg/cm^2 (a molecular weight of 27 has been assumed).

The value of T_s and y_1' have been obtained by using figure 17.

The experiments of Lake and Marklund have been performed using a tube 1.5 cm in diameter. In the decomposition zone, for T ≃ 1400 °K, our computation gives :

$$\mu = 0.562 \quad 10^{-3} \quad g/cm \ sec.$$

$$g\rho = \frac{981 \ p \ 10^3}{\dfrac{8136,6}{27} 10^4 \ 1400} = 2.325 \quad 10^{-4} \ p \ \frac{g}{cm^3}$$

and $$\nu = \frac{0.562 \quad 10^{-3}}{2.325 \quad 10^{-4}\ p} = \frac{2.417}{p} \ \frac{cm^2}{sec.}$$

p being expressed in kg/cm^2.

The value :

$$\nu = \frac{2.5}{p} \ \frac{cm^2}{sec}$$

is used below, although it is not clear whether the mean value in the decomposition zone or in the mean flow has to be used.

For T = 2000 °K , a rough estimate gives :

$$\mu = 0.77 \quad 10^{-3} \quad g/cm \ sec.$$

and $$\nu = \frac{4.73}{p} \ \frac{cm^2}{sec}$$

It is seen from equation (14) that y^*_{cr} varies approximately as the reciprocal of ν. The selection of a larger value would, therefore, decrease y^*_{cr} accordingly without influencing the subsequent computation, however.

Equation (14), with the preceding numerical values, gives :

$$\frac{V\, y_1'\, p}{14.375} = y_{cr}^{*} \left[0.30435 + \log_{10} 1.5\, y_{cr}^{*} + \log_{10} \frac{1}{y_1'} \right]$$

from which figure 18 has been computed, giving y_{cr}^{*} as a function of $V_{\perp}/V$ for the nine experimental points selected above.

Figure 18 shows that y_{cr}^{*} seems to be almost entirely determined by ratio $V_{\perp}/V$, velocity V and pressure p having only a minor influence. In the subsequent computation, therefore, the dotted mean line is used for approximating the dependence of y_{cr}^{*} on $V_{\perp}/V$.

It is interesting to remark that this dependence is very much influenced by the selected numerical value; in a preliminary calculation using :

$$Q_s^{o} = 36.32 \text{ kcal/mole oxidizer}$$

a simple relationship between y_{cr}^{*} and $V_{\perp}/V$ was hardly noticeable.

X X X X

The preceding results, obtained by correlating experimental data with theory, will be used in the following section for computing the influence of grain design and motor scale on erosive burning.

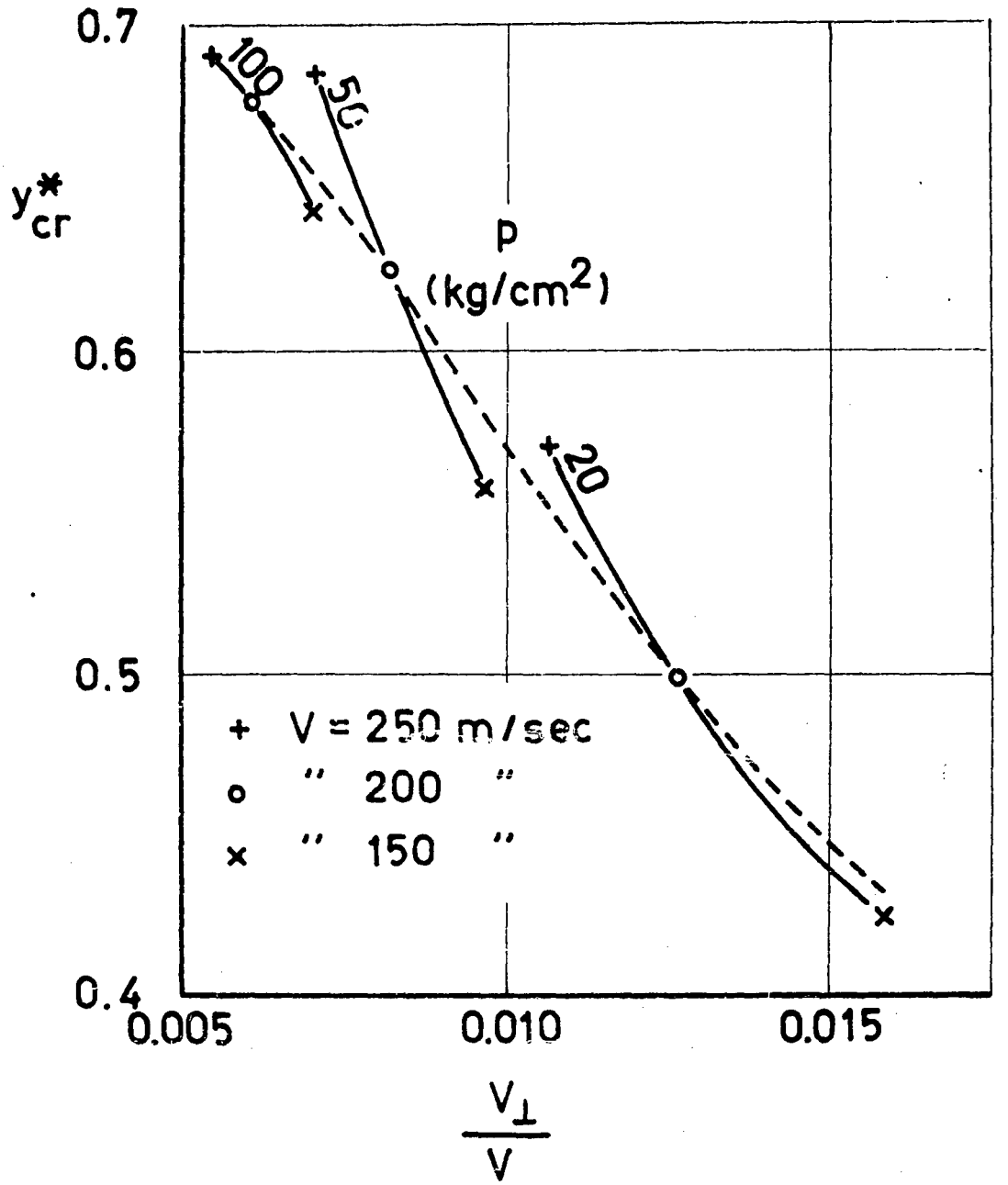

0.7
0.6
0.5
0.4
y^*_{cr}
100
50
20
p
(kg/cm²)
+ V = 250 m/sec
o " 200 "
x " 150 "
0.005
0.010
0.015
$\frac{V_\perp}{V}$

FIG.18

5. INFLUENCE OF GRAIN DESIGN AND MOTOR SCALE .

Experimental data discussed in section 3 - B suggest that local port dimension covers both the influence of motor scale (overall effect) and that of grain design (local effect).

Quantitatively the influence of local perforation dimension can be taken into account by replacing the pipe radius R in equations (11) and (14) by the local hydraulic radius R_h :

$$R_h = 2 \frac{\text{Cross-sectional area}}{\text{Wetted perimeter}} \tag{15}$$

In particular, at 70.3 kg/cm^2, equation (14) can be written:

$$\frac{V\, y_1'}{0.2045} - \left(0.30435 + \log_{10} y^*_{cr} + \log_{10} \frac{1}{y_1'}\right) = \log_{10} R_h \tag{14}$$

from which figure 19 has been computed.

It gives R_h as a function of y_1' for two particular values of the mean flow velocity V = 200 and 400 m/sec, taking into account the dependence of y^*_{cr} on V_1/V as given by figure 18.

The dependence of burning rate r on y_1' is also represented on figure 19 which serves as an auxiliary diagram for computing figure 20.

The relationship defining k_M can also be written :

$$\frac{r - r_o}{r_o} = k_M\, G/G^* \tag{16}$$

and for a given value of G/G^* (of V or M), in the presence of a sufficiently strong erosion, the proposed theory assumes that the burning rate is independent of r_o : it is expected, however, to depend on hydraulic radius.

Comparison between two cases differing by strand burning rate r_o and hydraulic radius R_h can be carried out using the following relationship :

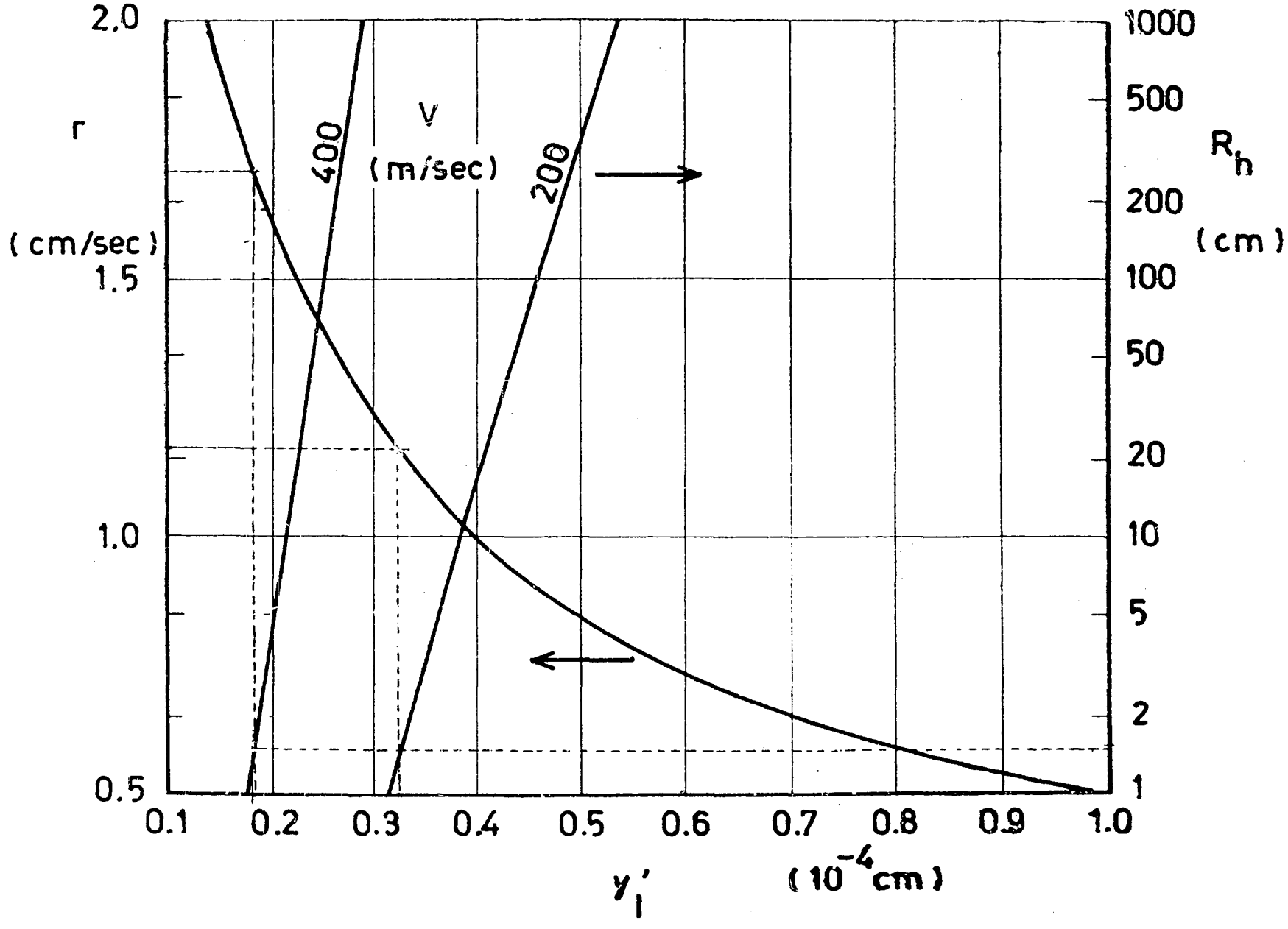

2.0
1.5
1.0
0.5
r
(cm/sec)
1000
500
200
100
50
20
10
5
2
1
R_h
(cm)
V
(m/sec)
400
200
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
y_1'
(10^{-4}cm)

FIG.18

$$\frac{r''_o\,(r' - r'_o)}{r'_o\,(r'' - r''_o)} = \frac{k'_M}{k''_M} \text{ for } G/G^*, V \text{ or } V \text{ given} \qquad (17)$$

the reference case being indicated by ' and the other one by ".

In the following computation no attempt is made to arrive at absolute values of the erosion coefficient k_M but rather to relative variations, assuming a reference point:

$r'_o = 0.65$ cm/sec

$k'_M = 1.00$

and $R'_h = 1.5$ cm.

at 70.3 kg/cm^2. These values are selected in accordance with Green's data for the purpose of obtaining a value of k'_M equal to unity:

The results obtained by Lake and Marklund suggest a larger value at that particular point while those of Fenech and Billheimer may apparently be interpreted as indicating a lower value (the motor dimensions and the pressure level corresponding to these experiments, however, are not reported) [13, 14, 17].

The computation of figure 20 can be carried out in the following manner:

a - for r'_o, R'_h and V given, the corresponding value of r' is obtained on figure 19 (see dotted line),

b - for V given, the values of r" corresponding to different values of R_h are obtained on figure 19,

c - for V given and arbitrarily selected values of r''_o, the corresponding values of k''_M are computed through equation 17.

Figure 20 shows that the erosion coefficient k_M decreases with increasing values of hydraulic radius R_h and of strand burning rate r_o.

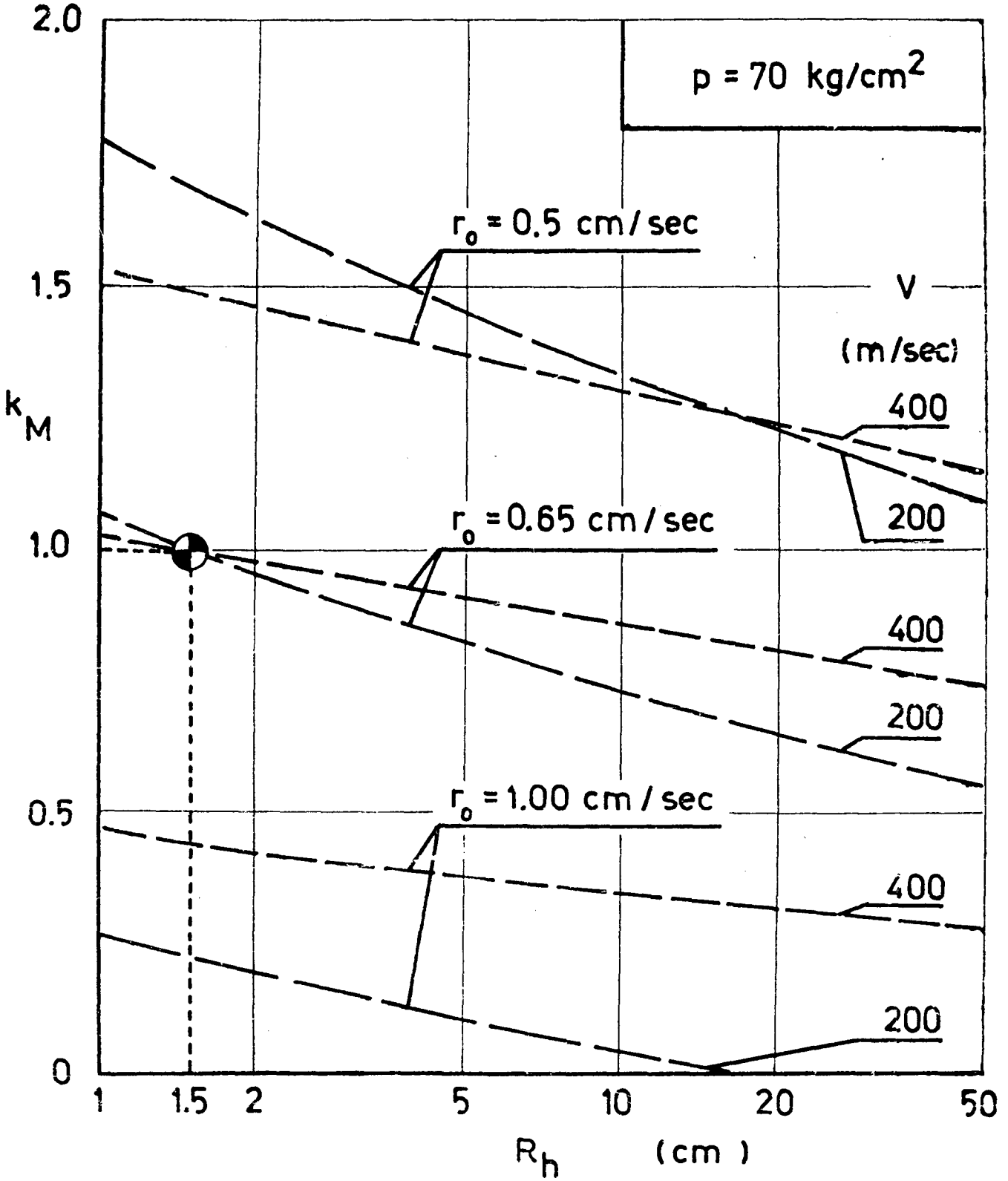

p = 70 kg/cm²
r₀ = 0.5 cm/sec
r₀ = 0.65 cm/sec
r₀ = 1.00 cm/sec
V
(m/sec)
400
200
400
200
400
200
k_M
2.0
1.5
1.0
0.5
0
1
1.5
2
5
10
20
50
R_h
(cm)

FIG. 20

The range of variation of k_M is apparently in relatively good agreement with the results of Fenech and Billheimer, although no definite conclusions can be drawn without complementary information on pressure level, motor scale and possibly ballistic modifiers [17] .

For fixed values of R_h, the dependence of k_M on r_o is normal : it results directly from the correlation for section 4-C-δ .

The influence of mean flow velocity V, however, must be discussed with the greatest caution ; it results mainly from the fact that equation (18) is an empirical approximation which poorly describes the phenomenon, and does not take into account the existence in certain cases, of the treshold velocity as discussed previously (the strand burning rate of the reference point has also been selected for the fact that it corresponds to a negligible threshold velocity in the interpolation of the results obtained by Lake and Marklund [1, 14]).

6. A TENTATIVE EXPLANATION OF IRREGULAR BURNING IN SOLID PROPELLANT ROCKETS.

Several excellent survey-papers have been presented recently by McClure, Price and others on the important and difficult problem of unstable burning in solid propellant rockets [29, 30].

Generally these authors emphasized the poor present understanding of the phenomena involved and the necessity to take into account the burning mechanism of the propellant.

For our purpose, their conclusions can be summarized as follows:

- under certain conditions, many but apparently not all propellants have the intrinsic ability to support oscillatory burning,
- actual initiation of oscillatory burning of an intrinsically unstable propellant results from an extremely delicate gain-loss energy imbalance which is influenced by a great number of factors,
- in many cases oscillatory combustion gives rise to irregular burning characterized by large and erratic variations in mean chamber pressure.

The desirability of a clear distinction between oscillatory and irregular burning complicates the problem and the greatest caution is imperative in this difficult matter. Recent progress in understanding the steady-state burning mechanism of ammonium perchlorate propellants (see section 4-A), however, have been sufficient for justifying a tentative phenomenological explanation for the intrinsic ability of a propellant to support oscillation and burn irregularly under certain conditions.

It seems reasonable, indeed, to expect that the surface erosivity, and possibly also acoustic admittance, in other terms the propellant response to small velocity and pressure perturbations is much larger for a smooth surface than for a rough one.

Moreover, roughness is not the only criterion, another most important surface characteristics being the nature of the protrusions. At low pressures, the surface protrusions are made of ammonium perchlorate which, alone, is a fair monopropellant probably capable of amplifying perturbations.

On the other hand, at high pressures, the apparent surface consists in fuel peaks generally made of rather inert substances whose regression can hardly be expected to be influenced much by small perturbations. This may not be true anymore, however, for active fuels such as nitrocellulose.

The discussion is summarized by figure 21 which reproduces experimental data obtained by Landsbaum, Kuby and Spaid [31] and gives the severity of irregular burning, as measured by the ratio of the increase in pressure to the normal chamber pressure, as a function of combustion to throat area ratio K which is itself a function of pressure (K = 100, 200 and 300, correspond respectively to $\overline{p}_c$ = 170, 390 and 710 psi). This figure also represents the type of surface which corresponds to the various behaviours, a nearly flat surface being assumed to give maximum instability.

One may be surprised by the sharp decrease in severity observed just above that particular pressure. A possible explanation is that, in this region, the rapid appearance of even a limited number of fuel peaks over the main surface almost completely prevents the establishment of small velocity oscillations over the active surface of the oxidizer.

The small amount of erosivity remaining in region D may be due to a few large crystals still slightly protruding (bimodal distribution) and in many instances the existence of this region has not been observed [31].

X X X

This theory assumes that small oscillations mainly affect the protrusions; it is consistant with the view that erosivity plays a predominant role in irregular burning described by Brownlee and Marble [32].

Although the acoustic admittance of the propellant can be also expected to depend on surface rugosity, this theory may not necessarily provide the complete explanation for oscillatory burning, and other factors, such as the gas-phase reactions, may have to be taken into account, as proposed by Barrère [24].

X X X

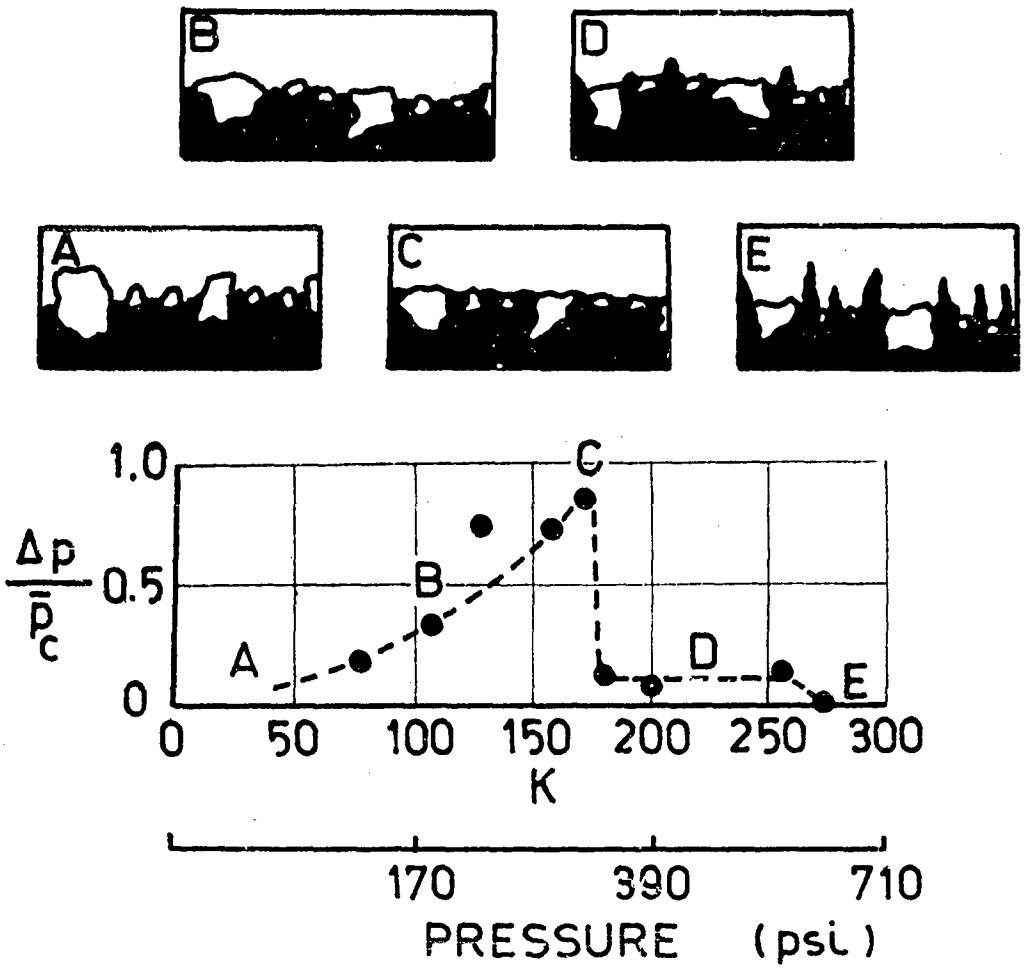

B
D
A
C
E
1.0
0.5
0
Δp / p̄c
A
B
C
D
E
0
50
100
150
200
250
300
K
170
390
710
PRESSURE (psi)

FIG. 21

Let us now discuss briefly some of the conclusions which can be drawn from this theory.

It can be shown easily, through comparison between burning rates of propellants and pure ammonium perchlorate, that an increase in oxidizer content or a decrease in crystal average size both result in a decrease in surface rugosity and a stronger tendency for the perchlorate to stay protruding above the surface, both factors favouring the ability to sustain irregular burning [19, 20].

Along these lines, the influence of aluminum powder in suppressing irregular burning could be explained, tentatively, by an increase in surface roughness through cratering and the detachment of crystals away from the surface, as observed by Barrère [24].

This theory may perhaps also be applied to other formulations: indeed the flat active combustion surface of double base propellants may explain the apparent absence of any particularly orderly dependence of severity of either oscillatory combustion or irregular burning on pressure, in tests on a variety of formulations [33].

On the other hand the systematic protrusion of fuel peaks over the burning surface of ammonium nitrate propellants may be the origin of their stable behaviour.

X X X

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66 pages and 21 illustrations.

ABSTRACT : After a critical survey of existing theories of erosive burning and of published experimental data, the combustion mechanism of ammonium perchlorate proppellants is discussed and a model of erosive burning of these formulations is proposed.

Erosion is assumed to smooth the surface whose burning rate is then controlled by oxidizer regression, no energy being supplied by the main diffusion flame. Furthermore the adiabatic decomposition temperature of the perchlorate is assumed to be obtained at the end of the laminar sublayer whose thickness can be related to mean flow velocity through fluid dynamics. Correlation of test data permits to determine the transition point. Grain design and motor scale are taken into account through local hydraulic radius.

Low pressures, large radii and high burning rates are shown to reduce erosive burning.

Finally an attempt is made for explaining irregular burning by surface nature and roughness, through erosivity.

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