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REPORT ON THE TEMPERATURE DEPENDENCE OF ROCKET BEHAVIOR

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REPORT ON THE TEMPERATURE DEPENDENCE OF ROCKET BEHAVIOR

ABSTRACT

Section I

It is pointed out that the temperature dependence of the pressure in rocket motors may be expected to be three to four fold greater than the dependence on temperature of the maximum pressure in guns.

This extreme temperature dependence is influenced by two independent characteristics of the propellant powder:

a. the value of the exponent, n, giving the pressure dependence of the burning rate, and

b. the temperature coefficient of the burning constant, b, itself.

The lower values of the exponent n, which favor low temperature coefficients of pressure, may possibly be favored by inclusion of certain catalytic materials in the powder.

Lower values of the temperature coefficient of the burning constant are favored by inclusion of dinitrotoluene in the propellant, which is explainable. It is suggested that the explanation may point the way to the search for materials of better characteristics having the same effect as dinitrotoluene.

Complete failure at extremely low temperature or pressures is presumably related to incomplete reaction of intermediate gases given off by the propellant. These failures may be obviated by inclusion of cobalt catalysts in the propellant composition. These catalysts may possibly have other desirable effects, such as reducing the exponent.

Unsatisfactory ignition, especially at low temperatures, may be avoided by using specially coated propellant grains.

Marker paints, which change color at the unsafe temperature extremes could be used to reduce accidents.

Some experiments upon which these deductions are based are described in greater detail. These include:

Section II

Evidence to support a picture of the mechanism of burning as follows:

1. Heat supplied by subsequent reactions and conducted back to the solid propellant surface liberates, by an endothermal process, some highly reactive gas or gases. This process proceeds at a rate determined only the rate at which heat is supplied and controls the overall burning rate.

2. These gases, when present at sufficient pressure, react rapidly with one another or with material on the solid surface of the propellant with liberation of sufficient heat to sustain reaction (1). The significant products of this reaction are a white solid and probably NO_2. This reaction goes to completion at pressures of 1.5mm or more.

3. The products formed in stage (2) react further, if the pressure exceeds about 10mm to produce gaseous and liquid products. Among these products the thermally significant materials are nitric oxide and incompletely oxidized organic compounds, specifically aldehydes. This reaction is essentially completed at something less than atmospheric pressure.

4. This reaction, which has been most studied, consists in the oxidation of combustible organic products from reaction (3) by nitric oxide, and is much more sluggish than the other preceding reactions. This step releases about one-half of the energy of the overall reaction and is therefore important. Because it is so sluggish, this reaction is believed to have no effect on the overall burning rate, which is probably controlled by steps (1) and (2) or by (1),2 and 3.

Section III

Titanium-potassium perchlorate mixture coated on the outside of powder grains is shown to reduce the time required to ignite powder. Comparison with uncoated powder seem to indicate that at low temperatures the burning is more complete and rapid with the coated powders.

Section IV

The integrated thrust time divided by charge weight for the 2.36" rocket, as a function of charge weight, at approximately constant temperature, is found to be constant above a certain charge weight. Below this charge weight the total thrust per unit charge drops rapidly, indicating incomplete combustion.

SECTION I

General

Some experimental work on the mechanism of propellant combustion has been underway for some time at the Ballistic Research Laboratory. Only very recently has a project been undertaken looking to the improvement of the performance of the 2.36" rocket at high and low temperatures. As a consequence, the experimental work performed which is directly concerned with the temperature dependence of rocket behavior, is extremely meagre. On the other hand, the results of the previous more fundamental studies on the mechanism of burning, have colored the approach to the temperature dependence problem. This report concerns itself largely with projected and hopeful fields of investigation rather than with accomplished experiments.

It is customarily assumed that the linear rate of regression of a powder surface, $\mathring{Z}$, is a function of the temperature of the powder, and of the external pressure, alone. Certain exceptions to this will be discussed later. The dependence of $\mathring{Z}$ on pressure may always be approximated by the equation

$$\mathring{Z} = bP^n \tag{1}$$

where $\underline{b}$ is a function of the powder temperature. (It is not intended to imply here that the "power" law (1) is inherently superior to another frequently used approximation, $\mathring{Z} = a + bP$, which may represent a better fit for some powders).

The number $\underline{n}$ in equation (1) has a value of approximately 0.85 for many powders. Since the rate of egress of gases from the nozzle is proportional to P, the equilibrium pressure, P_e, for powder of constant burning surface, would be proportional to the $1/(1-n)$'th power of the burning constant, $\underline{b}$,

$$P_e \sim b^{1/(1-n)} \cong b^7 . \tag{2}$$

Since the maximum pressure in a gun is rather closely proportional to b^2, it is seen that the temperature coefficient of the pressure in a rocket motor may be three to four fold the coefficient for the maximum gun pressure.

As far as choice of propellant is concerned, the improvement in rocket behavior at extreme temperatures is to be sought by either or both of two methods

(a) to decrease $\underline{n}$
(b) to decrease the temperature dependence of the burning constant $\underline{b}$.

In regard to method (a), the following may be said:

A change of n from 0.85 to 0.70, without alteration of the temperature coefficient of the burning rate b, will halve the temperature coefficient of the equilibrium pressure.

Theoretical considerations indicate that n probably depends on the effective order of the gas reaction in the intermediate products leaving the powder surface. If this order were unity n should be 0.5, if the order were two n should be unity. Sufficiently little is known of the mechanism of this reaction to make it improbable that theoretical considerations alone would, in the near future, enable us to predict the dependence of n on composition. There remains, however, one possibility. Certain catalysts for the gaseous reaction may be expected to more likely decrease than increase the order of the reaction. The inclusion of such catalysts in the powder, which is desirable for other reasons discussed later, may possibly have an effect tending to decrease the temperature coefficient of the pressure. Such little information as has been obtained here as yet on possible catalysts is discussed in section (II) of this report.

There is little coherent experimental information on the effect of chemical composition on the exponent n. It does appear that the Russian powder containing dinitroluene (DNT) has lower n than the usual American composition. It has been reported (orally) that the ammonium picrate-sodium nitrate alternate propellant of N.D.R.C. section 8 has n = 0.4.

In regard to the method (b), the reduction of the temperature coefficient of the burning constant itself, the following may be said:

It is frequently assumed that the burning constant b is inversely proportional to the heat necessary to bring the powder from its initial temperature into the gas phase in the form of some intermediate products. For pure nitrocellulose this heat may consist almost entirely of the integrated specific heat over the temperature of about 200°C. For such a case $b = b_o/(T_i - T)$ where the constant, T_i, of dimensions of temperature will be approximately equal to the ignition temperature.

If the powder contains some relatively stable component which volatalizes unchanged in the initial decomposition of the solid, this heat will include the heat of vaporization of this material. Such a material is DNT which has been recovered unchanged from the products of partial burning. In this case b will be inversely proportional to

$T_i + \Delta H - T$ where the ΔH term is proportional to the heat of vaporization of the stable component. The rate, b, will be lowered and the temperature coefficient decreased. DNT is known experimentally to decrease burning rates and temperature coefficients.

Were the stable component to contain a better oxygen balance than DNT the heat liberated in the subsequent gaseous reaction would tend to partially offset the effect of the extra heat of vaporization in lowering the rate, but would still leave temperature coefficient low. There appears to be reason to seek such a component which would be satisfactory for inclusion in powders.

It has been assumed that the burning rate is determined by the initial powder temperature and the external gas pressure alone. Experimental confirmation of this viewpoint is inadequate. Indeed some evidence exists that it is not, in all cases, correct.

One minor effect, which is understandable, may be mentioned. The heat conductivity of the powder is certainly low compared to the burning rate, and presumably a steady state temperature distribution is rapidly set up in which the temperature of the solid a few hundredths of a millimeter in from the burning surface is essentially that of the initial powder. This will, however, only be the case if the powder is opaque to radiation. If transparent, the radiation from the burning gases will continually heat the main body of the powder, and the burning rate would be expected to increase explicitly with time. This effect would be independent of fissure formation, although presumably related to it.

The "chuffing" occurring in rockets at low loading densities indicates that the burning rate depends on other factors than $\underline{P}$ and initial temperature. It appears that this chuffing occurs only under conditions in which the reaction characterizing the burning does not go to completion. A complete satisfactory explanation of chuffing is not at hand, but it is believed that the phenomenon is intimately connected with the incomplete reaction.

It is believed that the burning proceeds in steps, the last of which is the oxidation of certain organic materials, probably largely aldehydes, by nitric oxide. This step goes only slowly except at highly elevated pressures. The heat liberated in the incomplete burning, when the last step does not take place, is only roughly half the normal value for complete reaction. At low pressures, and indeed even at pressures but little lower than those occurring in some rockets under operating conditions, this reaction is so slow that incompletely reacted gases are ejected at the nozzle.

The evidence for this belief lies in plots of the total integrated thrust per unit charge consumed, against loading, for the 2.36" rocket. At high loadings, for which the burning pressure is high, the thrust per charge weight is constant, independent of the loading. As the loading decreases a marked break occurs, the thrust per unit charge decreasing precipitously with decreased loading. This decrease begins when the running pressure is about 1500-2000 p.s.i.

It is believed that the inclusion of catalysts containing cobalt, or possibly other catalysts, might sufficiently speed the slow end reaction to permit complete burning at lower pressures. This would extend downwards the temperature limit for normal (although slow) burning for given design and loading.

It is also contemplated that such catalysts might increase the normal burning speed by bringing the "burning layer" of gases closer to the powder surface, and possibly decrease the temperature dependence of the pressure by decreasing the burning law exponent n.

There appears to be a considerable delay period between the firing of the igniter and the true ignition of the powder. This delay period is markedly increased at low temperatures. It appears that powders coated with a titanium-potassium perchlorate mixture ignite more readily and uniformly than uncoated powders. It is hoped that improved ignition may be obtained and might result in improved performance.

Finally the use of paints which change color at the dangerous temperature extremes may be used to color rockets in such a way as to reduce accidents.

SECTION II

Experiments on Burning of Cellulose Nitrate

The simplest hypothesis capable of accounting adequately for the observed behavior of burning propellants requires that the process consist of at least two steps. These are first, the conversion of the solid propellant to a mixture of gases, (an endothermal process) the energy consumed by this conversion being furnished by the second step, the highly exothermal subsequent reaction of these gases to form the final products of the reaction.[1]

This suggested that the attempt be made to decompose the powder thermally, removing the gaseous products rapidly enough and at a sufficiently low pressure to prevent their reacting further. Under these conditions it should be necessary to supply energy continuously to maintain the decomposition. The experiment was tried by placing a strip of cellulose nitrate in the neck of a large flask evacuated to a pressure of 0.01 m.m. of mercury, and concentrating the radiant energy from a rod-shaped heating element on the powder with an elliptical mirror. The powder was decomposed slowly, as shown by the rise of pressue which was measured by a MacLeod gauge. The rate of evolution was quite slow, and ceased when the source of heat was removed. This decomposition could be continued for long periods of time provided that the pressure in the flask was maintained below 1.5 m.m. by suitable pumping.

The moment, however, that the pressure rose above this value, and regardless of whether the cellulose nitrate was a fresh strip or one that had previously been heated for some time, the decomposition became self-sustaining and would continue after removal of the heat until the powder was completely consumed. The products of this rapid decomposition were not gases only, but gases plus a white solid. Chart No. 1 presents the results of two such experiments in which pressure in the flask is plotted against time.

A series of experiments was next made in which weighed quantities of powder were subjected to this rapid decomposition not in vacuum but in various pressures of argon and carbon dioxide, and the resulting increases in pressure used to calculate the amounts of gas evolved per gram of cellulose nitrate consumed. These data are plotted in Chart No. 2. The amounts of cellulose nitrate decomposed were so chosen that the increase in pressure on decomposition was small compared to the initial pressure, and hence the difference in volumes of gas evolved between the three points at lowest pressures may well be experimental error.

1 J. E. Mayer, "Preliminary Report on Propellant Burning", Ballistic Research Laboratory.

Up to 5 m.m. initial pressure of carbon dioxide, or 10 m.m. of argon, an approximately constant volume, viz. 175 c.c. of gas per gram of cellulose nitrate, is evolved. At higher pressures the volumes of gas evolved per gram of cellulose nitrate increase rapidly, and the amounts of the white solid decrease. When the initial pressure of inert gas had been increased sufficiently to yield approximately 500 c.c. of gas per gram of cellulose nitrate, no more of the white solid was to be seen, and instead the products were entirely gases and liquids. Among the latter aldehydes were always prominent. Nitric oxide was also always prominently present, and since this gas is (in the practical sense) the most stable of all the oxides of nitrogen, these facts suggest that the final reaction in propellant burning consists in the oxidation by nitric oxide of the aldehydes and other organic compounds probably present) to yield the final products of the burning.

It may be mentioned here that when we burned propellant powders containing D.N.T. under these conditions, a part at least of the D.N.T is recovered unchanged.

In order that the reaction might be consummated at higher pressures, and also that we might follow the heat evolved as an additional index of the completeness of the reaction, succeeding experiments were performed in a Parr calorimeter. The density of loading as well as the initial pressure of inert gas was varied, and Charts Nos. 3 and 4 show the calories evolved per gram of cellulose nitrate consumed, as a function of the density of loading. Each curve is labeled with the inert gas used and its pressure. One feature common to all of these curves except that for 10 atm. of argon is that there is a region throughout which increase in the density of loading causes a decrease in the heat of explosion. This was investigated in the following way. An additional series of runs was made in each of which 25 c.c. of 0.1008 N phenylhydrazine solution was introduced into the bottom of the bomb. After firing, the reaction products were allowed to react with the phenylhydrazine, whose excess was then titrated. The consumption represents most probably aldehydes and ketones. These runs were made in the presence of 1 atm. of CO_2, and it will be seen that the curve representing c.c. of phenylhydrazine consumed per gram of cellulose nitrate has a horizontal portion at approximately the same density of loading at which the heat of explosion curve has a minimum. This lends a slight additional reasonableness to the heat of explosion curve, although the role of these aldehydes is not at all clear.

Finally, a series of runs was made in each of which 0.50 grams of cellulose nitrate was used, and the initial pressure of carbon dioxide varied from 1.0 to 62.2 atm. In addition to measuring the heat evolved, samples of gas were withdrawn and analysed for nitric oxide and nitrogen. Because of the extensive dilution of the reaction products by the initially added carbon dioxide, the results of these analyses are not too accurate, but can, we be [illegible] be taken as substantial confirmation of the hypothesis that the final reaction is

$$\text{aldehydes, etc.} + (2x + y)NO \rightarrow xCO_2 + yH_2O + (x + y/2)N_2$$

The results of this series of experiments are given in Table I.

It may be mentioned that although all of the work reported here is done on cellulose nitrate, Bryce Crawford after learning of our results obtained the same general behavior with double base powders.

To summarize the evidence so far presented, we think it is very probable that the burning of propellants takes place in the following steps.

(1) Heat supplied by subsequent reactions and conducted back to the surface of the solid propellant liberates by an endothermal process some highly reactive gas or gases. This process proceeds at a rate determined only by the rate at which heat is supplied.

(2) These gases, when present at a sufficiently high pressure, react rapidly with one another or with material on the solid surface of the propellant with liberation of heat sufficient to sustain reaction (1). The significant products of this reaction are a white solid and probably NO_2. This reaction goes to completion at pressures of 1.5 m.m. or more.

(3) The products formed in step 2 react further to produce gaseous and liquid products. Among these products the thermally significant materials are nitric oxide and incompletely oxidized organic compounds, specifically aldehydes. This reaction is essentially complete at something less than atmospheric pressure.

(4) This reaction, which has been most studied, consists in the oxidation of combustible organic products from reaction (3) by nitric oxide, and is much more sluggish than the other preceding reactions. This step releases about one half of the energy of the overall reaction, and is therefore important. Because it is so sluggish, this reaction is believed to have no effect on the rate of the reaction, which is probably controlled by steps (1) and (2), or by (1), (2) and (3).

It might be thought that the densities of loading at which this final reaction is incomplete are so small as not to represent anything likely to occur in practice. It must be remembered, however, that in these bomb experiments the reaction products are confined, and continue to react at declining rates as the temperature falls. In a rocket on the other hand, the gases are retained in the motor chamber for a time much shorter than this and may react very incompletely under conditions of temperature and pressure that would have resulted in complete reaction in a bomb. As a matter of fact, we have invariably found these aldehydic intermediates in cases of bad malfunctioning of rockets.

TABLE I

Initial PCO_2, atmospheres	Heat of explosion, cal./gm.	NO in gas vol. %	N_2 in gas vol. %
1	530	30.4	11.1
14.6	611	15.8	19.3
28.2	630	11.1	22.9
62.2	988	0	29.4

The conditions outlined here indicate a search for a catalyst capable of promoting the reaction (4). A search of the literature unearthed no previous work on catalysts for oxidations by nitric oxide, so one can only guess at what such a catalyst might be. The "catalysts" listed in the table below were all investigated in the following way. A 0.5 gram sample of cellulose nitrate when burned in our bomb releases 530 cal/g. in the presence of 1 atm. of carbon dioxide. A 0.8 gram sample releases 725 cal./g. Each catalyst tried was mixed dry with powdered cellulose nitrate in a concentration of 2%, and 0.5 gram and 0.8 gram samples fired in the bomb and the resulting heats of explosion recorded. If the catalyst showed promise, it was also tried in a concentration of 0.5%

TABLE II

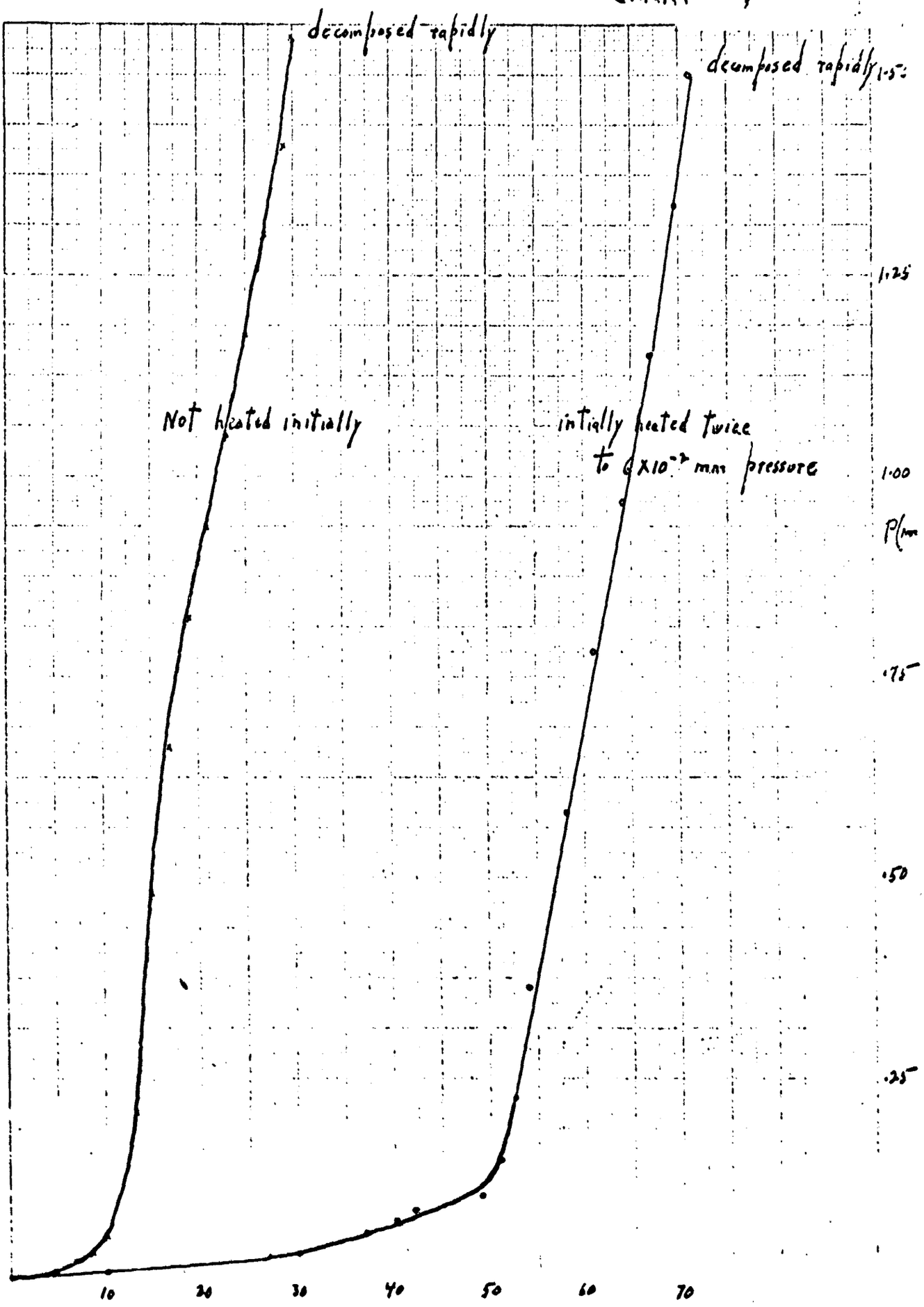
Catalyst	% by Wt. in nitrocellulose	Wt. sample, gms.	Heat of Explosion cal./gm.
$HgCl_2$	2	.5	507
	2	.8	512
CuCl	2	.5	582
		.8	903
$CH_3C_6H_4SO_2Cl$	2	.5	575
		.8	928
CrO_2Cl_2	1 drop	.5	986
		.8	1008
$MoO_2Cl_2H_2O$	2	.5	562
		.8	942
$CoCl_2$	2	.5	598
		.8	1029
MoO_3	2	.5	797
		.8	1038
	0.44	.5	567
		.8	1015
$K_2Cr_2O_7$	2	.5	943
		.8	978
	0.44	.5	572
		.8	1032
Cr_2O_3	2	.5	538
		.8	1000
TiO_2	2	.5	494
		.8	580
ZnO	2	.5	567
		.8	580
$KClO_4$	2	.5	860
		.8	1041
	0.5	.5	548
		.8	1012

Catalyst	% by Wt. in nitrocellulose	Wt. sample, gms.	Heat of Explosion cal./gm.
CoC_2O_4	2	.5	548
		.8	901
$Co_3(PO_4)_2$	2	.5	495
		.8	657
$Co(ClO_4)_2$	2	.5	1098
		.8	1040
	0.5	.5	875
		.8	1048
Co soap	2	.5	557
		.8	848
Pb soap	2	.5	557
		.8	1042
Co resinate	2	.5	713
		.8	1095
	0.5	.5	567
		.8	622
Mn resinate	2	.5	542
		.8	549
Rosin	2	.5	530
		.8	715

Of the "catalysts" listed, it is quite plain that a number (CrO_3, $KClO_4$, etc.) exert a beneficial effect merely by furnishing oxygen. Even a small percentage of oxygen is advantageous since the temperature of the reacting gases is thereby raised to the point at which the NO decomposes sufficiently rapidly to support further reaction. On the other hand, salts of cobalt exert an effect which seems to be truly catalytic. Among these the cobalt salt of abietic acid, cobalt resinate, seems to be outstanding. Here a word of explanation is necessary. This substance was prepared here in the laboratory by heating cobalt oxide with rosin, extracting and dying. It showed on analysis only 0.3% cobalt, about 1/30 of the expected percentage of cobalt. The percentages of catalyst recorded are percentages of this impure material, and should be divided by thirty for fair comparison with the other catalysts if the effective ingredient is really cobalt abietate. An experiment was run with added rosin, which was totally ineffective. Hence the preparation of pure cobalt abietate seems indicated. A single attempt to prepare the nickel abietate was unfortunately unsuccessful.

Cobalt perchlorate was also particularly effective, as might be expected. Unfortunately, most of these catalytic investigations were made in the week immediately preceding the writing of this report and are still in progress.

CHART #1


decomposed rapidly
decomposed rapidly
Not heated initially
initially heated twice
to 6 X10⁻² mm pressure
1.50
1.25
1.00
P(mm
.75
.50
.25
10
20
30
40
50
60
70
Time (min.)

NO. 340-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH
EUGENE DIETZGEN CO.
MADE IN U.S.A.

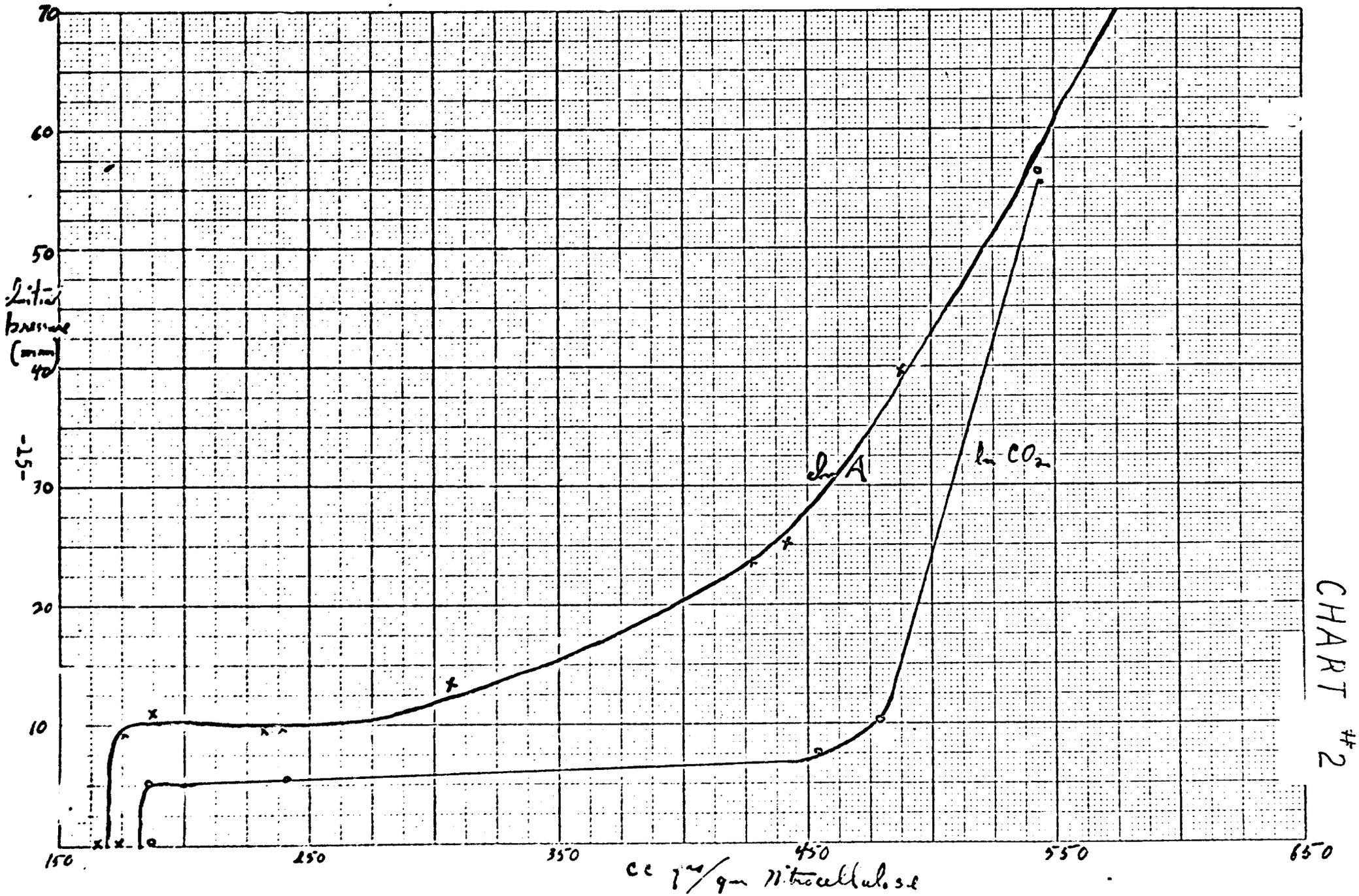


CHART #2

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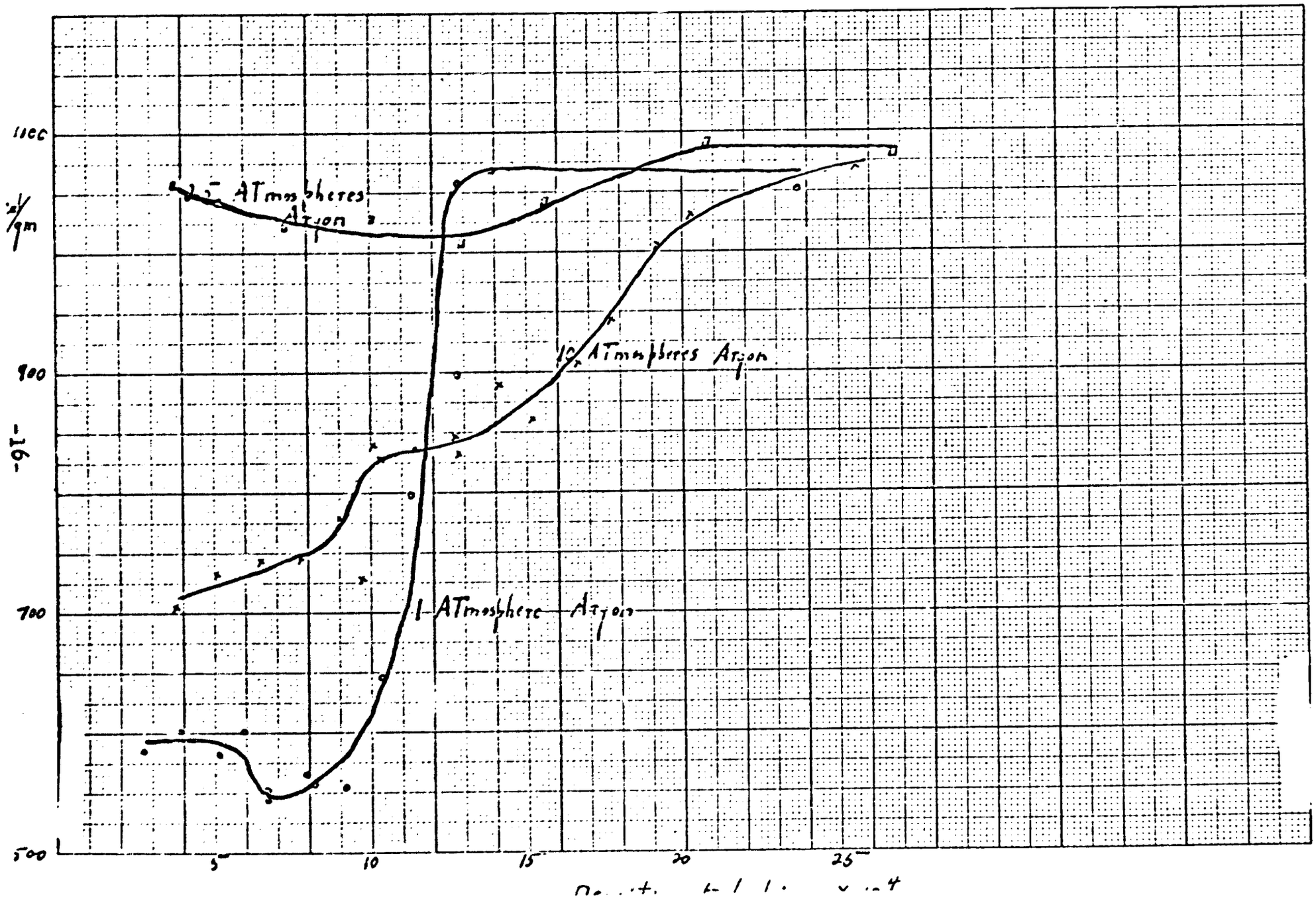

CHART #3

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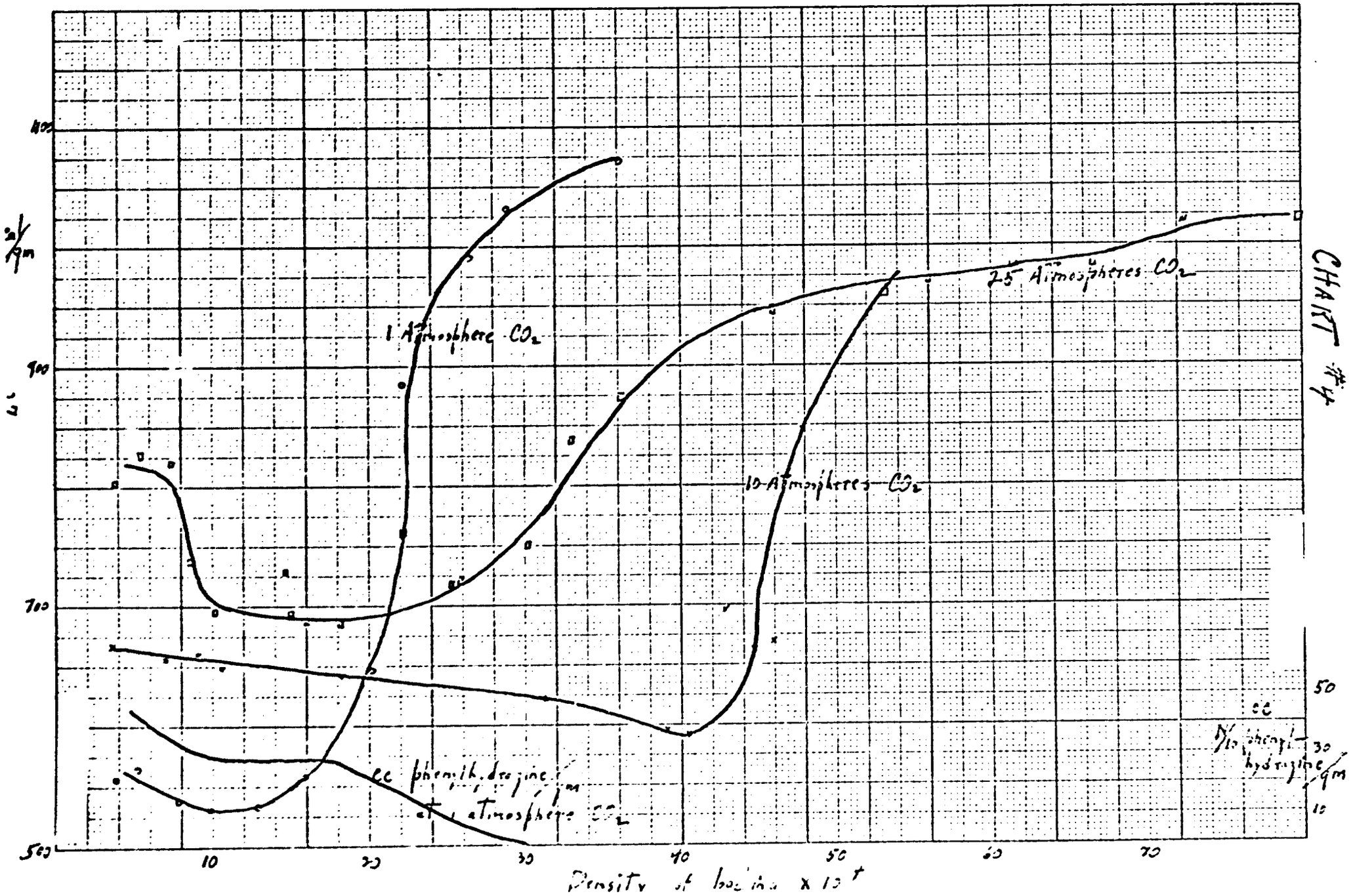

SECTION III

Closed Chamber Experiments with Coated Powders

A. Summary

Ineffective "ignition" has been suggested as one of the possible causes of malfunctioning of rocket powders. A series of closed chamber experiments made at 21°C (room temperature) and about -40°C, showed that rocket powder grains, which had been coated with a mixture of titanium and potassium perchlorate, were much easier to ignite than uncoated grains.

At about -40°C misfires were avoided by coating the grains. At 21°C, the powder grains, which had been coated, were ignited and burned completely during a time period which was one-fourth to one-half as long as the corresponding time period for the uncoated grains. This decrease in time required for ignition and burning caused by coating was accompanied by no more than a slight increase in the maximum pressure observed within the closed chamber. Comparison of the results obtained at -38°C and at 21°C with coated bazooka powder grains showed that the rate of burning was substantially the same at the two temperatures. The pressures observed in the closed chamber on firing coated grains at -38°C were only a few per cent less than the pressures observed at room temperature. It is concluded that applying a coating of titanium-potassium perchlorate mixture to powder grains renders their ignition easier, quicker and less temperature dependent. As a result the burning rate is probably also less temperature dependent.

B. Purpose

This work was undertaken to determine whether the time required for ignition and burning of rocket powder at room and subzero temperature could be shortened by applying, to the surface of the powder grains, a composition consisting mostly of titanium and potassium perchlorate.

The conclusions are based on experiments made at room temperature and only two experiments at about -40°C. The two experiments were made on the day before this report was written. Unfortunately, time has not yet permitted adequate substantiation of these results.

C. Experimental Work

(a) Coating the Powder Grains

The powder grains were coated as evenly as possible with a composition consisting mostly of a mixture of powdered titanium

(two atomic weights) and powdered potassium perchlorate (one molecular weight). The coating process consisted of first softening the surface of a powder grain by brief immersion in ethyl acetate, then rolling in a thin layer of small flakes of the titanium-potassium perchlorate composition, manipulating the coated grain so as to secure adherence of the titanium-potassium perchlorate flakes and finally heating for at least 16 hours at 80°C to volatize the ethyl acetate. The flaked titanium-potassium perchlorate composition consisted of 10 parts of titanium-potassium perchlorate mixture and 3 parts of double base rocket powder as a binder. Further details as to the coating procedure are given in Appendix I.

The powder grains were conventional double base rocket propellants. The amount of coating composition amounted to about 2.2% of the powder weight for the bazooka powder and about 0.8% for the 4.5 rocket grains.

(b) Closed Chamber Firing

The closed chamber used was a steel cylinder closed at both ends by threaded plugs. The chamber was fitted with a piezo-electric gauge of standard design. On firing the weighed powder sample, the electrical charge generated by the piezo-electric gauge is amplified, and caused to deflect the spot on a cathode ray (oscillograph) tube. The position of the moving oscillograph spot is recorded on a continuously moving photographic film. The firing of the powder charge was carried out electrically by sending a current of several amperes through a fine tungsten wire in contact with a small roll of single base nitrocellulose powder in thread form. One gram of thread powder was used in each firing.

In making runs at about -40°C dry ice was used to cool the closed chamber and the powder sample. In these experiments, the powder sample was placed inside the chamber before the dry ice was applied to the outside of the chamber. The temperature was determined by means of a thermocouple placed inside the powder grain (all the powder grains tested had one axial perforation). During the cooling period, the opening threaded to receive the piezo-gauge was closed by a plug so as to avoid freezing the gauge. Just before making the firing, the piezo-gauge was screwed into place. The rest of the firing was done in the usual way.

Allowance was made for the temperature rise of a few degrees centigrade which occurs during thefew minutes required to screw in the piezo-gauge and make the electrical connections preparatory to firing.

The low temperature (about -40°C) was reached either by cooling directly from room temperature until the thermocouple indicated a temperature of slightly below -40°C or by keeping at dry ice temperature (about -65°C) for several hours, then removing the closed chamber from the dry ice and allowing the temperature to rise gradually to about -40°C. The first method of cooling was used with the coated bazooka powder and the second with the coated powder for the 4.5 rocket.

The maximum pressures were computed from the oscillograph record using the well established, standard methods. The oscillograph record gives, essentially, the pressure as a function of the time measured in milliseconds. The point in time, at which the switch was closed to ignite the thread powder, is also recorded on the oscillograph record. The time elapsed from the instant of closing of the ignitor switch to the instant at which the pressure curve reaches its maximum has been taken as the "Ignition and Burning Time (Total)". Values for the "Time Required for Pressure to Rise from 10% of Maximum to the Maximum Value" were also read from the oscillograph record and are given in Tables III and IV.

The chemical analyses and grain dimensions of the powders used in these firings are given in Table V.

D. Discussion of Results

Before attempting to evaluate the results, it seems advisable to establish a criterion for judging the significance to be attached to the various values of pressure and burning time. Table VI presents data obtained on making six repeat firings at room temperature with single base powder in which all conditions were kept identical, as far as possible, and in which the pressure and time measuring technique was the same as that used in the firings reported in Tables III and IV. This single base powder was 155mm. howitzer "green bag" charge and was in the form of single perforated grains of 0.0165" web thickness. Data presented in Table VI show that the average of the pressure deviation is 1.41% of the average maximum pressure, while the average deviation in time of ignition and burning is 9.05% of the average value.

The data in Table III show that coating the bazooka powder with the titanium-potassium perchlorate composition has a number of effects. The coating decreased the total ignition and burning time at 21°C by 74% of that observed with the uncoated powder. The maximum observed pressure at 21°C was increased by 7%. The data are regarded as too meagre to attach any significance to the differences in time required at 21°C for the pressure to rise from 10% of the maximum to the maximum value. The failure of the uncoated powder grains to fire at -38°C indicates the greater ease of ignition of the coated grains under adverse conditions. Attention is directed to the fact that, at -38°C, the pressure developed was only 6.5% less than at 21°C. Work by Dr. R. B. Dow of the Ballistic Research Laboratory had led us to expect that the maximum pressure at -38°C would be approximately one-half of that at 21°C. It is not known at present whether the surprisingly high pressures obtained at -38°C with the coated grains is due entirely to improved ignition or to other effects. Investigations on this point are in progress. The ignition and burning time of the coated bazooka grains increased from an average of 0.313 seconds at 21°C to 0.431 seconds at -38°C. The time required for the pressure to rise from 10% of maximum to the maximum value was nearly the same at -38°C as at 21°C for the coated bazooka powders. Further experiments will be needed to establish

whether significance is to be attached to the observed differences caused by the lower temperature in the burning time and on the time for the pressure to rise from 10% of the maximum to the maximum value.

Data relative to the effect of the titanium-potassium perchlorate coating on ignition and burning of propellant for the 4.5 rocket are presented in Table IV. The effect of the coating on the maximum pressure developed at -38°C was the same as with the bazooka powder. The effect of lowering the temperature from 21°C to -40°C on the ignition and burning time of the coated 4.5 rocket grains was larger than that observed with the coated bazooka powder. An explanation of this difference might be sought in the possibility that at the time of firing a lower temperature may have prevailed in the web of the 4.5 powder grain. It is recalled that the 4.5 powder was held at about -65°C for several hours, while the bazooka powder was not.

APPENDIX I OF SECTION III

Coating of Powder Grains

The material used for coating the powder grains was prepared as follows. Powdered titanium (obtained from Metallic Hydrides, Inc., Beverly, Mass.) and potassium perchlorate (Fisher's, CP) were dried separately for at least four hours in an oven kept at 80°C. 139 grams of potassium perchlorate (corresponding to one gram molecule) were weighed out and carefully ground by hand in a mortar. The ground potassium perchlorate was then mixed with 95.8 grams of powdered titanium (corresponding to two atomic weights of this metal). This mixing was carried out by using a spatula to mix and turn the titanium and potassium perchlorate spread out on a sheet of kraft paper. It is not believed advisable to use grinding equipment, e.g., mortar and pestle, to effect the mixing of the titanium and the potassium perchlorate due to danger of setting off the material. 40 grams of the titanium-potassium perchlorate mixture were mixed with eight grams of double base rocket powder dissolved in about 35 c.c. of acetone to form a soft doughlike mass. More acetone was added from time to time during the mixing to keep the mass plastic and workable. The composition was then diluted to a thin paste with acetone, spread out in thin streaks on plate glass and allowed to dry. The dried streaks were scraped off in the form of flakes. These were screened using a piece of copper fly screen of about 20 mesh per inch. The flakes passing through the screen were used to coat the powder grains.

Before actually coating the powder grains, a thin, nearly continuous layer of the titanium-potassium perchlorate flakes was spread out on kraft paper. A powder grain was then submerged in ethyl acetate for about two seconds, then withdrawn, allowed to drain briefly and then rolled at once in the titanium-potassium perchlorate flakes spread out on the kraft paper. The flakes were brought into intimate contact with the powder grain by marking with the fingers. The powder grain was then allowed to dry for a few minutes and flakes which were not firmly held removed by rubbing the grain surface with the fingers. With a little practice, this technique produces a

powder grain almost completely covered with a firmly bonded coating of flakes of titanium-potassium perchlorate mixture. The coated grains were then allowed to dry at least 16 hours in an oven heated to 80°C for the purpose of driving off ethylacetate.

The interior of the axial perforation of the powder grains was not coated with the titanium-potassium perchlorate composition.

TABLE III

Effect of Temperature on Time of Ignition and Burning of Bazooka Powder

Firing No.	Powder Lot No.	Coated or Uncoated	Temperature of Firing	Maximum Pressure Developed lbs./sq.in.	Ignition and Burning Time (Total)	Time Required for Pressure to Rise from 100% of Maximum to the Maximum value
4264	10976	Uncoated	21°C	5032	1.376 secs.	0.0565 secs.
4263	10976	Uncoated	21°C	5131	1.040 secs.	0.055 secs.
4281	10976	Coated	21°C	5400	0.275 secs.	0.061 secs.
4291	10976	Coated	21°C	5234	0.351 secs.	0.0635 secs.
4274	10976	Uncoated	-38°C	Failed to fire		
4284	10976	Coated	-36°C	4969	0.431 secs.	0.058 secs.

TABLE IV

Effect of Temperature on Time of Ignition and Burning of Propellant for 4.5 Inch Rocket

Firing No.	Powder Lot No.	Coated or Uncoated	Temperature of Firing	Maximum Pressure Developed lbs./sq.in.	Ignition and Burning Time (Total)	Time Required for Pressure to Rise from 100% of Maximum to the Maximum Value
4283	9971	Uncoated	21°C	4861	0.624 secs.	0.123 secs.
4282	9971	Coated	21°C	5184	0.375 secs.	0.121 secs.
4292	9971	Uncoated	-40°C	Failed to fire		
4301	9971	Coated	-38°C	4708	0.652 secs.	0.137 secs.

TABLE V

Analysis and Grain Dimensions of Rocket Powders

Analysis

	Bazooka Powder (Lot 10976)	4.5 Rocket Powder (Lot 9971)
Nitrogen content (of nitrocellulose omponent)	13.23%	13.24%
Nitrocellulose	58.79%	58.26%
Nitroglycerin	40.56%	40.54%
Ethylcentralite	-----	1.01%
Diphenylamine	0.65%	0.19%
Total Volatiles	0.37%	0.67%
Moisture	0.51%*	Not given
Ash	0.6 %	0.5 %

*Moisture content exceeds maximum permitted which is 0.40%.

Grain Dimensions (In Inches)

	Bazooka Powder (Lot 10976)	4.5 Rocket Powder (Lot 9971)
Length	4.76	5.149
Diameter	0.371	0.878
Perforation	0.06	0.272
Number of Perforations	1	1
Web Thickness	0.155	0.3030
Density	1.63	1.62

TABLE VI

Accuracy of Reproducibility of Closed Chamber Data

Firing No.	Maximum Pressure Developed lbs./sq.in.	Deviation from Average Maximum Pressure lbs./sq.in.	Ignition and Burning Time (Total)	Deviation from Average Ignition and Burning Time
4141	4474	77	0.199	0.033
4142	4342	55	0.225	0.007
4143	4266	131	0.209	0.023
4144	4457	60	0.270	0.038
4145	4418	21	0.234	0.002
4146	4425	28	0.255	0.023
Average	4397	Average 62	Average 0.232	Average 0.21

Average of pressure deviation is 1.41% of average maximum pressure.

Average of ignition and burning time deviation is 9.05% of average ignition and burning time.

SECTION IV

Static Firing at Reduced Loadings

A. Summary

The practice rocket grenade (the 2.36" rocket) was fired statically at reduced loading, and thrust-time measurements were obtained. Normal type of equations were obtained for burning rate vs average thrust and average thrus vs. k, the ratio of powder area to throat area. However, a plot of the area under the thrust-time curve per unit weight of powder, a measure of the momentum released by the powder as a function of loading, shows an abrupt falling off of available energy for charges below of normal charge. This decrease of released momentum is accompanied by the appearance of reaction products within the rocket body after firing.

The important variables in rocket design which affect the burning of the propellant are the weight of propellant used, its dimensions, the ambient temperature, the area of the nozzle, interior dimensions of the rocket, and the type and size of the igniter. This report presents a brief study of the effect of weight or propellant used, the other factors remaining nearly constant.

B. Experimental Work

The practice rocket grenade, T11, using an aluminum covered electric squib as igniter, was statically fired at loadings from normal, 65.0 grams, down to 22% of normal. Thrust-time records were obtained in each case, together with visual observations. The powder used was standard.double base rocket grenade powder having the specifications:

Nitrocellulose (13.25%N)	59.25 ± 2.00
Nitroglycerin	40.00 ± 2.00
Diphenylamine	0.75 ± 0.10

Immediately after each firing the rocket grenade was opened and the interior examined. In several cases, unburned powder was present, and such powder was weighed to determine the amount of powder burned. Motion pictures were taken of each firing with a 120 frame per second camera. The results are presented in Table III, and certain values plotted in Figures 5, 6 and 7.

C. Discussion of Results

An examination of Table III shows that as the loading was reduced, a point was reached at which the powder was only partially burned. Further reduction causes a series of "chuffs", with increasing consumption of the powder,

until the powder is all consumed. Further reduction results in a smaller number of "chuffs" of decreasing intensity. Accompany these effects, is the appearance of residues within the rocket after firing. These residues included material of aldehydic nature.

Figure 5 shows the area under the thrust time curve per unit of powder as a function of the initial weight of powder At about the same loading that partial burning is found, the momentum released falls off sharply. This effect agrees with the presence of reaction products as indicating an incomplete type of reaction. It may be noted that the ordinates in this figure correspond to $\int Pdt/k$, which Golden (NDRC A-97) has theoretically shown to be a constant for normal operation.

On the other hand, plots of the burning rate as a function of average thrust, Figure 6 and average thrust as a function of k, Figure 7, show no discontinuities in these regions. Data of Golden (NDRC A-97), for the same kind of powder in the rocket grenade, are plotted on these figures and agree very well.

When unburned powder was recovered, the appearance of the powder corresponded to that reported by English workers (AC 1050) as to the waviness of surface, and increased burning of the end of the powder grain at the closed end of the rocket.

D. Conclusions

Reduced loading of the rocket grenade gives results comparing closely with those obtained at normal loadings as far as burning rate and average thrust are concerned. The total momentum released per unit weight of powder falls off abruptly, however, in a definite region as the loading is reduced. Since, however, the length of burning time has attained its maximum, before this region of partial burning is reached, it may be expected that this region will not enter into a study of the normal rocket grenade. Long burning itself gives unsatisfactory operation since the operator's face will be burned.

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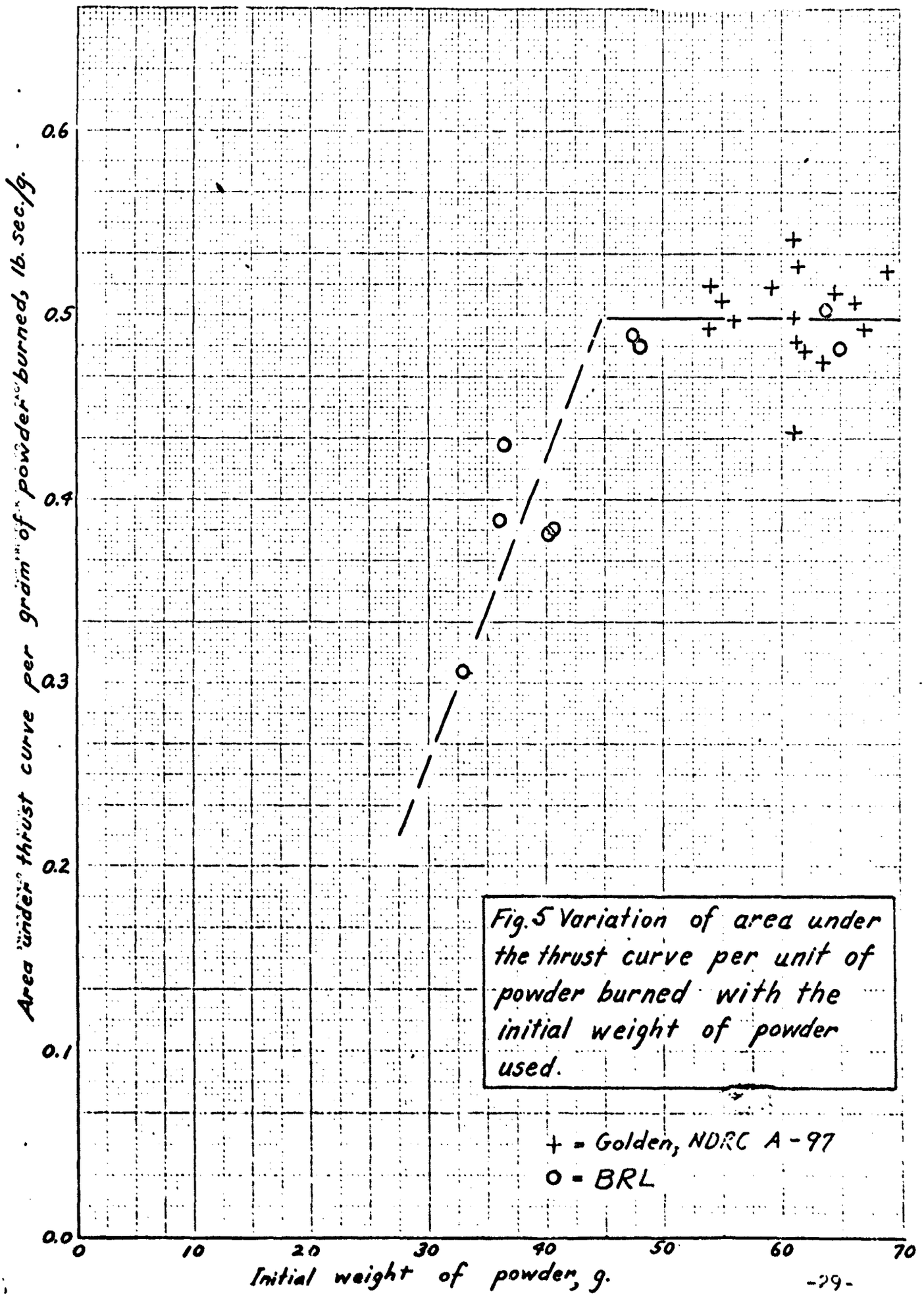

Fig. 5 Variation of area under the thrust curve per unit of powder burned with the initial weight of powder used.

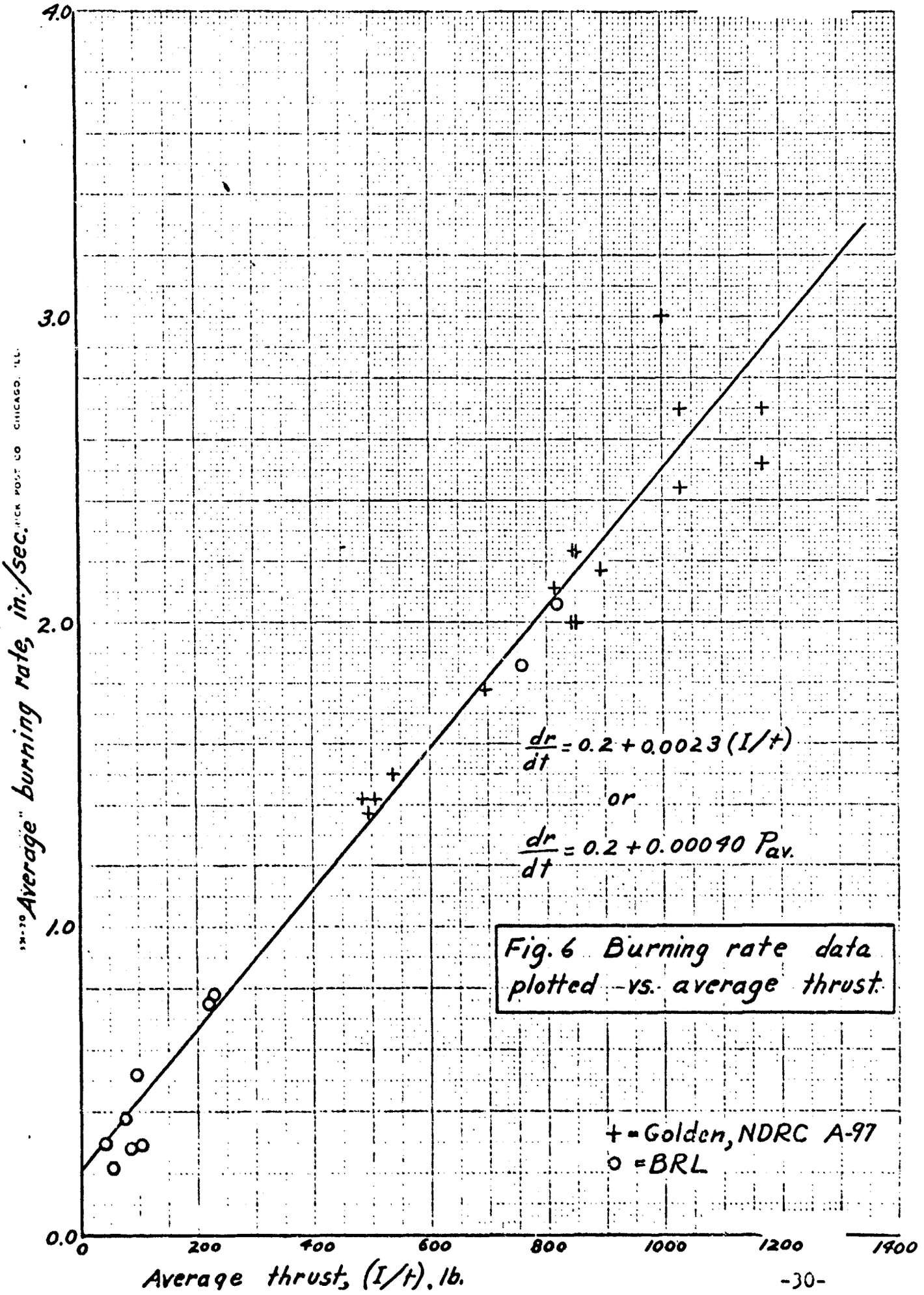

Fig. 6 Burning rate data plotted -vs- average thrust.

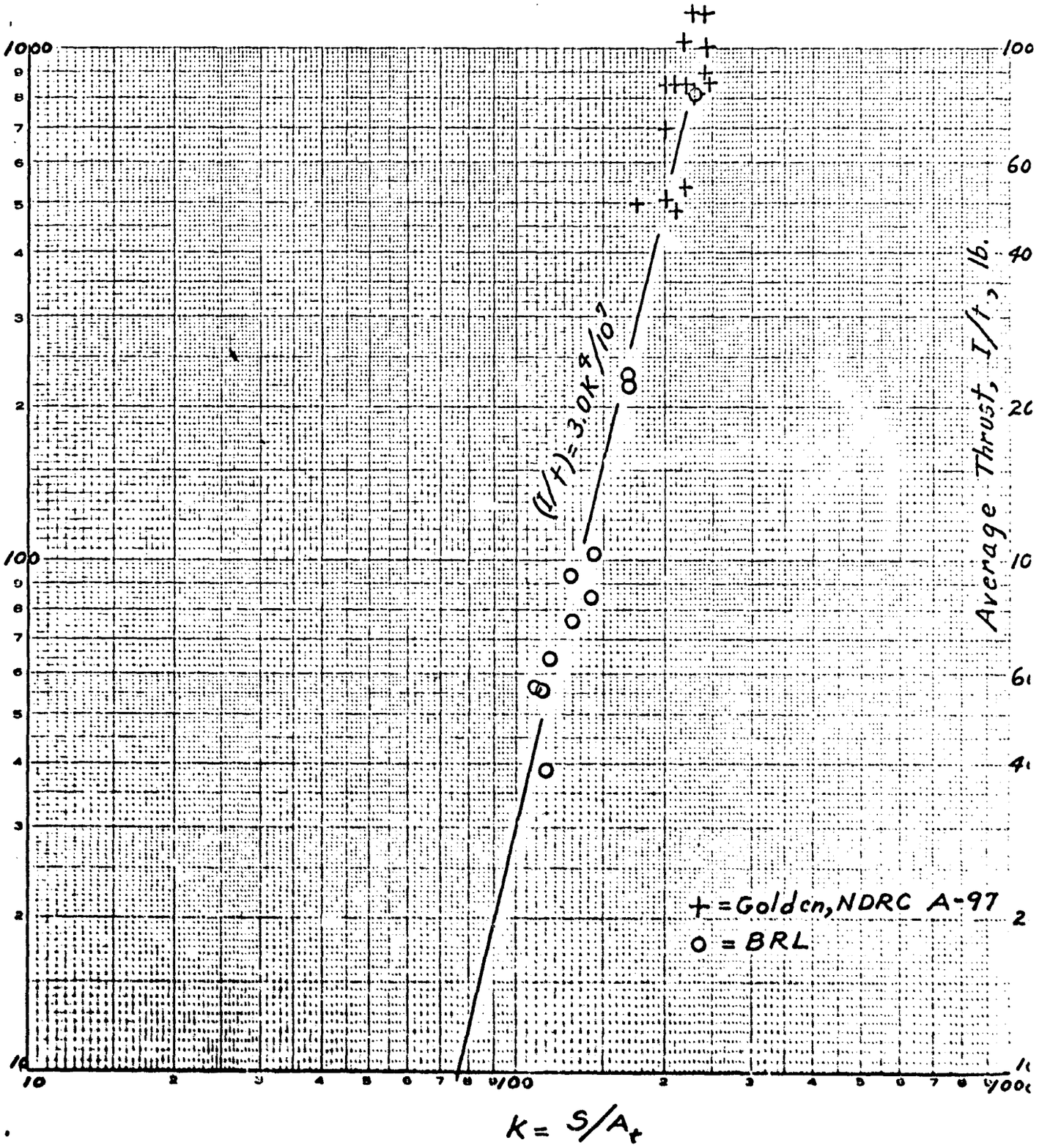

Fig. 7 Variation of average thrust with K.

III

g of 2.36 in. Rocket Grenade, at 60-70°F.

Burning rate in/sec	$k = \frac{A}{A_t}$	REMARKS
0.44	143	Initial pop of primer followed by loud chuff.
0.52	144	
	130	First flash followed four light chuffs.
	128	Flash of flame. Deposit of aluminum powder on inside of rocket.
	124	Flame on first and fifth chuffs only. Small amount of smoke on other chuffs.
—	111	First four chuffs loud, with flame, last three not loud, with no flame. Some oily type of deposit on inside of rocket.
—	117	First and seventh chuffs loud, with flame. Initial chuff preceded by slight chuff sound, probably due to primer.
	100	After each chuff, small cloud of yellow grey heavy smoke rolled out.
2.06	231	Rocket very clean inside after loud chuff.
1.86	227	" " " " " " "
0.75	171	Interior of rocket quite dirty with black deposit after chuff.
0.73	169	" " " " " " " " " "
0.52	129	
0.38	130	Aluminum dust on retaining ring. Heavy grey smoke inside after chuff.
0.30	115	Dirty nozzle after chuff. Walls have oily deposit. Heavy yellow smoke inside.
—	112	First and fifth chuffs loudest. Other chuffs gave a deal of smoke.
—	83	Nozzle dirty and walls have oily deposit.
—	86	First and third chuffs gave flame. Last chuff very feeble with a streak of flame appearing about one ft. from nozzle.
—	52	Feeble chuffs. Considerable oily residue on walls and nozzle very dirty. Heavy yellow smoke inside.
—	52	Puff of flame on first chuff. All chuffs feeble. On last chuff, streak of flame appeared about foot from nozzle. Very dirty inside.

the first number indicates the blast number.

ken of all such blasts.

the data. This was necessary due to the vibration of the thrust bar.

of k.

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Temperature dependence of pressure in rocket engines is greater than in guns. Temperature dependence is influenced by pressure rate of burning and temperature coefficient of burning constant. Dinitrotoluene is added to propellant. Incomplete reaction of gases causes complete failure at extremely low temperatures and pressures. Coated propellant grains avoid unsatisfactory ignition. Integrated thrust time divided by charge weight for 2.36 in. rocket was found constant above certain charge weight.

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b. BRL Report ~~391~~ 343 DJM, "Heats of Explosion of Nitrocellulose in Indifferent Atmospheres (Part 1 of Mechanism of Powder Burning)", by J. H. Frazer and C. P. Fenimore, August 1943, UNCLASSIFIED.

c. BRL Report 353, "Report on Temperature Dependence on Rocket Behavior," by J. H. Frazer et. al., May 1943, UNCLASSIFIED.

d. BRL Report 465, "Experiments on Ignition of Nitrocellulose", by C. P. Fenimore and J. H. Frazer, May 1944, UNCLASSIFIED.

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