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DIVISION 8

NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

CAST PERCHLORATE PROPELLANTS BASED ON
THERMOSETTING HIGH POLYMERS

Explosives Research Laboratory

OSRD Report No. 5582
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Endorsement from Dr. Ralph Connor, Chief, Division 8 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee. Forwarding report and noting:

"Since the physical properties of long chain high molecular weight polymers change much less rapidly with temperature than do those of pitchy or asphaltic materials, it seemed possible that the useful temperature range of the Galcit propellants might be extended by replacing the asphalt binder in these propellants with suitable long chain high molecular weight polymers.

The present report describes the development, the preparation, and the properties of a cast perchlorate propellant based on a Permafil resin. Although the development was not completed because of the termination of hostilities, sufficient work has been done to show that this propellant has the desirable qualities of the Galcit propellants and is not subject to the temperature limitations of those propellants."

This is a progress report under Contract OEMsr-202 with the Carnegie Institute of Technology.

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Progress Report

OSRD No. 5582

on

"Cast Perchlorate Propellants Based on
Thermosetting High Polymers"

from the

Explosives Research Laboratory
Bruceton, Pennsylvania

Investigation Group:

J. E. Ablard
G. B. DeLaMater
H. F. Hardman
F. P. Price
H. H. Young

Report prepared by: Report approved by:

H. F. Hardman   Louis P. Hammett
G. B. DeLaMater   12 November 1945

Summary

The Galcit propellants developed at the California Institute
of Technology are outstanding in their ease of preparation
and in the simplicity of the equipment in which they are pre-
pared. Compared with many propellants they have the further
major advantage of a low temperature coefficient. They have,
however, shown deficiencies when used at very high or very
low temperatures of a kind which are probably unavoidable
in a material of a pitchy or asphaltic nature. Such materials
become soft enough to flow at high temperatures and become hard
and brittle at low ones. Work in this laboratory on binders
for composite propellants (OSRD Report No. 5586) had shown
that long chain high molecular weight polymers and especially
elastomers have physical properties which are much less sensi-
tive to temperature than are pitches and tars. Consequently
investigation was started the latter part of 1944 looking
toward the development of a castable propellant composed of
a mixture of potassium perchlorate with some suitable high
polymeric material.

It was clear from the beginning (Section IIB) that the most desirable material would be one which is initially a liquid of moderate viscosity and which can be converted after casting into a rubbery polymer by chemical action at not too high a temperature. Materials of these properties are not familiar and common products of industry, particularly when the added demand is made that they should not shrink too largely during the polymerization and that the initial material should not be highly volatile. Consequently the earliest development involved a thermoplastic material composed of ethylcellulose and castor oil (Appendix A). While this material in a 25:75 ratio by weight with finely ground potassium perchlorate showed some advantages over the Galcit composition and was further improved in its ballistic properties by the addition of 5% aluminum, it was still subject to definite limitations in the temperature range over which it may be used. In February of 1945 M. M. Safford of the General Electric Corp. suggested the use of thermosetting elastomers of the type represented by the General Electric Permafil resins. These are initially sufficiently fluid to permit casting a mixture containing from 75 to 80% of potassium perchlorate at room temperature. In the presence of a peroxide catalyst the mixture sets up overnight at 60°C to a low strength gel about the consistency of art gum. In its polymerized condition it has no flow at 60°C and it is still a rubber-like material at -40°C. The perchlorate-Permafil composition can be prepared by a simple mixing and casting technique, there appear to be no limitations on the size of charge that can be made, and softening at high temperatures or brittleness at low ones do not limit the range of temperature over which it can be used. The raw materials appeared to be available even under war-time stringencies at prices which were not prohibitive, and no heavy machinery such as presses or rolls would be necessary for fabrication. The propellant appeared therefore to offer excellent prospects for a rapidly available supplement to the limited existing supplies of fuels for jet propulsion applications. The early laboratory investigations were very promising; consequently arrangements were made in June to construct a small pilot plant for further study of the preparation and properties of the material at the Allegany Ballistics Laboratory. The plans for this plant, whose construction stopped with the cessation of hostilities, are described in OSRD No. 5584.

Further study on the laboratory scale at ERL developed some difficulties which had been largely but perhaps not completely eliminated when work on the project ended in October 1945. End-burning charges of the composition exhibited a very marked progression in pressure as burning went on (Sections IIB and IIC-1). This was found to arise partly from a relatively rapid burning of the propellant near the walls which resulted in the formation of a conical surface with the apex at the center of the charge. This increase in surface was not, however, sufficient to account for all of the increase in pressure and it appears that a pitting of the surface on a rather fine scale was responsible for approximately half of the effect. By a surprisingly small change in the composition of the resin the cone formation was eliminated and the progression due to pitting decreased somewhat. For the final composition the total progression during an 8 sec. time of burning amounted to 53% which is undesirably large but probably not prohibitive. Rather limited experiments indicate strongly, however, that forming of the initial burning surface into a cone or some other shape which tends to introduce regression into the burning can yield a charge of essentially neutral burning properties (Section IIH).

Restriction of the burning surface of the charge was not difficult at room temperature or higher, but it was only near the close of the work that what appears to be a satisfactory method of restriction for low temperature firings (-40°F) had been developed (Section IIG). This involves the application of a rubber sleeve under tension to the cylindrical surface of the grain which has previously been coated with an elastic thermosetting resinous composition which after cure adheres firmly both to the rubber and to the material of the grain.

At the time work on this project ceased (October 1945) it appeared probable but not fully demonstrated that a perchlorate-Permafil cast charge suitable for long burning airplane assisted take-off and similar applications could be produced in quantity; and that this charge would have reproducible ballistics, would show as low a temperature coefficient of pressure, burning time, and thrust as any available propellant and would be usable at least over the temperature range of -40 to +140°F. It could be produced from materials available in large quantities at moderate price in simple apparatus which would make the construction of a large production plant practicable under the war time shortage conditions.

Section III of this report gives detailed information on the properties of a recommended composition; Section IV outlines the probable process of manufacture; Section V makes recommendations of directions which further work should take if the development of this propellant appears desirable under peacetime conditions.

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I. Introduction.

There are available as materials which might be used with potassium perchlorate to yield a castable propellant two types of high polymers, the thermosetting and the thermoplastic. Polymers of the thermosetting type, once cured to the final state, are in general insoluble, infusible, and show extremely slight tendency to flow at any temperature. Thermoplastic polymers, on the other hand, have a definite melting range and flow slowly at temperatures considerably below this melting range.

Two manufacturing processes are possible depending on whether a thermosetting or thermoplastic resin is used.

1. If a suitable thermosetting resin can be found which consists in the initial state of a solventless liquid of moderate viscosity, the process would consist of mixing the liquid resin with $KClO_4$ at room temperature, casting at room temperature or after warming slightly, and finally curing at a moderate temperature to form the solid propellant.

2. In case a thermoplastic resin is used both the mixing and casting would be done at a temperature at which the resin is fluid (probably well above 100°C). On cooling a solid propellant would be obtained.

In view of the complete lack of flow of the cured resin at any temperature and the fact that throughout the mixing and casting process the temperature need not be above room temperature, while during curing it need be only moderately high (e.g., 60°C), it is obviously preferable to use a thermosetting resin matrix, both from the point of view of obtaining desirable properties in the final propellant and of making the process of manufacture less complicated and less hazardous. This project has been chiefly concerned with developing a cast perchlorate propellant based on a thermosetting resin, although some work has been done with one of the thermoplastic type.*

Three ways are apparent for restricting the burning to the desired surface in the case of end-burning solid cylinders and centrally-burning perforated charges. These are:

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*See Appendix A.

1. Bonding the propellant to the metal walls of the motor directly or through an interposed liner layer. The uncured propellant would be cast directly into a suitably prepared chamber and the bonding brought about as the result of the cure of the resin. The motor wall itself or the motor wall with the liner would serve as the restriction.

2. Bonding the propellant to some sort of non-metallic container which would serve as the restriction. Containers might be made of plastic, cork, fiber, paper, etc.

3. Applying a restrictive coat of the type used with composite propellants (e.g., primary paint coat plus industrial tape) to grains which have been cast and cured in a removable mold.

Inasmuch as the properties to be sought in the resinous matrix depend on which of the three methods of restriction is used an early decision had to be made on this point. The third method, that of applying a primary paint coat plus industrial tape to a molded grain, was selected* partly because of the experience acquired at this laboratory with such a coating on composite propellants. Further advantages in this choice were that the resinous matrix need not be one which would adhere strongly to metal surfaces and need not have as small a shrinkage during cure. Of equal importance was that grains could be inspected before coating and at various stages of the coating process. The equipment required and the manufacturing process was, however, made more complex by this choice.

It should be emphasized that the work described in this report is incomplete. At the time hostilities ended a pilot plant was being constructed which would have made possible the preparation of 900 lbs. of propellant per eight hour shift (OSRD Report No. 5584). However, this pilot plant was not completed because of the cessation of hostilities and the smaller scale experimental work has been stopped in an incomplete state. The chief need from this point in the development is for pilot plant scale experimentation.

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*Some work has been done with restrictions of the other types. This is described in Appendix B.

II. Experimental Development.

Because some of the more important applications for this type of propellant would require a large end-burning solid grain, most of the experimental work has been done using a sub-caliber grain four inches in diameter and eight inches long. The ratio of length to diameter of this grain is about that which would be required for a 1,000 lb. thrust 12 sec. unit or a 2,000 lb. thrust 30 sec. unit. Moreover, it proved to be a convenient size for casting and general handling. Later work emphasized 8-1/2" diameter solid grains, 6" long.

Throughout this work the single outstanding fault has been progressive burning. Early in the development it was found that pressures consistently increased more than 200% during burning and partially-burned grains were obtained from the interrupter burner whose burning surfaces, instead of being flat, were projecting cones having included angles of 90° to 100°. The surfaces of such cones are 30-40% greater than the initial surface, corresponding to pressure increases of 140-205% if the exponent n is 0.70. Plate 10 is a photograph of some partially-burned grains showing the conical surfaces formed. The conical surfaces were approximately surfaces of revolution, and so it was possible to estimate their apparent area by the method of Section II-A of this report. Comparison of the quantity

$$P_f/P_i \Big/ (A_f/A_i)^{\frac{1}{1-n}}$$

as calculated from these measurements with its theoretical value of $\underline{1}$ showed that the pressure increase was in general about twice that which would be predicted from the surface change. In addition then to the effect due to the increase in apparent area a second phenomenon, a small scale surface increase called "pitting", and possibly a third, a free space effect, contributed to the progressive burning. The term "apparent area" is used to describe the burning surface without regard for the additional surface due to pitting, including only the contribution due to change in overall surface contour.

Experiments which were successful in substantially reducing the surface change and the other effects are described in Sections II-B and II-C. The surfaces finally obtained showed only a general irregularity rather than a conical shape and so the method of estimating apparent areas was not as useful. A quantity useful in evaluating quality in the later stages of the development has been the progression in per cent per inch burned, defined as

$$\text{Prog. } \%/\text{in} = \frac{P_f - P_i}{P_i \times 1} \times 100$$

where P_f is the final pressure, P_i is the initial pressure, and 1 is the burning distance. P_f and P_i are measured from the pressure-time trace.

It has in general not been possible to make use of K-P plots to compare batch quality, since only a very few grains could be obtained from any one batch.

In studying composition variables, very valuable data have been obtained by the use of the Crawford burning rate bomb. The technique of making strands for firing in the bomb is described in the following section.

Test motors, nozzles, and the interrupter burner and its operation have been described in OSRD Report No. 5583.

A. Special Experimental Technique.

1. Estimation of Apparent Areas of Partially-Burned Grains.

The surfaces considered are approximately surfaces of revolution and may be considered as being made up of a series of elements, each one of which is the frustrum of a right circular cone. The surface of such an element is given by the product of the slant height, s, and the sum of the perimeters, P and p. (See Figure 1.)

$$A_{surface} = s/2(P+p) = S/2(2\pi R + 2\pi r) = \pi s(R+r)$$

The projected area of the frustrum is an annular ring of area.

$$A_{projection} = \pi R^2 - \pi r^2 = \pi(R^2 - r^2) = \pi(R+r)(R-r)$$

The ratio of the area of the frustrum to the area of its projection is given by

$$\frac{A_{surf.}}{A_{proj.}} = \frac{s}{(R-r)}$$

This ratio is equal to the secant of the angle, α (Figure 1). So,

$$A_{surf} = A_{proj.} \sec \alpha$$

The total area of the surface of revolution is given by

$$A_{total} = \sum A_{proj.} \sec \alpha$$

If the projected area of the surface is divided into n elements of equal area (the elements may be sectors rather than complete frustrums),

$$\frac{A_{surf.}}{A_{proj.}} = \frac{A_1 \sec \alpha_1 + A_2 \sec \alpha_2 + - - - - - - - + A_n \sec \alpha_n}{A_1 + A_2 + - - - - - - + A_n}$$

$$= \frac{\sec \alpha_1 + \sec \alpha_2 + - - - - - - \sec \alpha_n}{n}$$

since $A_1 = A_2 = A_3 = - - - - - = A_n$

This is the average of the secants of the angles of each of the elements.

The actual measurement of the apparent surface is carried out as follows: Three profile views at 60° to each other are obtained by shadowing the grains on translucent paper and tracing the outline so produced. The profile views are each divided into ten segments by ruling lines parallel to the axis of the grain, these lines being so located that when they are rotated about the grain axis they generate four annular rings and a central disk of equal area. The circular projection of the burning surface is thereby divided into thirty elements of equal area (see Figure 1).

The slope of each of the ten segments of the three profile views is measured with a specially constructed protractor which indicates directly the secant of the measured angle. The numerical average of these readings is the ratio of the apparent burning surface (neglecting smaller irregularities) to the cross-sectional area of the grain. The apparent burning area is computed by multiplying this ratio by the cross-sectional area of the grain.

From these profile views is obtained also an average $h_c - h_o$, the elevation of the highest point of the burning surface above the periphery.

2. Use of the Crawford Burning Rate Bomb.

The closed bomb technique for measuring burning rates has been described by Crawford and Huggett ("Direct Measurement of Burning Rates by an Electric Timing Method", OSRD Report No. 4009). Strands were prepared by pouring the uncured propellant into a glass mold 8"x6"x1/8". A sheet of cellophane was placed in contact with the surface exposed to air and the propellant hardened by heating 24 hours at 60°C. The sheet so formed was cut into strips 1/8"x1/8"x8" and these were given four dipped coats from a solution of (75-25) Castor Oil-Ethocel in toluene. After drying, the strips were dusted with talc to permit handling.

Measurements of burning rate were made at pressures between 500 and 2000 psi, and logarithmic plots of burning rate against pressure obtained. n is the slope of the graphically esti-mated best straight line.

3. Measurement of Viscosity of Uncured Propellant
Apparatus.

The measurement of viscosity is made with a simple apparatus in which the material is caused to flow through a tube of known dimensions under a constant pressure. The material which flows during a measured time interval is collected and weighed. The apparatus is shown schematically in Figure 2.

The reservoir is an 8" length of 2" steel pipe closed at the bottom end by a reducer into which may be screwed discharge tubes of various sizes. A 3/8" standard pipe nipple 5" long reamed to 0.500" inside diameter was found to cover the range of viscosities encountered. The upper end of the reservoir is fitted with a screwed-on flange to which may be bolted a flange bearing two rubber tube connections.

A mercury manometer attached by means of a rubber tube to one of the connections on the cover flange measures the air pressure in the fuel reservoir.

A large compressed gas cylinder containing air under slight pressure (in this work from 25 to 70 cm Hg) provides pressure to force the material through the outlet tube. The large tank acts as ballast, preventing any appreciable drop in pressure during a run. The hydrostatic pressure due to the height of the fuel surface above the discharge outlet is included in the calculations.

Treatment of Data.

The following equation* applies to the streamline flow of plastic materials (a class to which many suspensions belong) in cylindrical tubes.

$$\Delta P = \frac{16 \tau_o L}{3D} + \frac{32 \eta VL}{g \ D^2}$$

where:

ΔP = pressure drop, lb/ft^2.

L = length of pipe, ft.

g = conversion factor = 32.174.

τ_o = yield shearing stress = lb/ft^2.

η = rigidity, lb (mass)/ft.sec.

V = mean velocity, ft/sec.

D = diameter of pipe, ft.

*Perry, Chem. Engrs'. Hdbk. 2nd ed., p.820, McGraw-Hill Book Co., N.Y. (1941).

Multiplying by 3D/16L the equation becomes:

$$\frac{3D \triangle P}{16L} = \widetilde{\mathcal{C}_o} + \frac{6V \eta}{g D}$$

The plot of $3D \triangle P/16L$ against $6V/gD$ is a straight line having a slope of η and a y-axis intercept of $\mathcal{C}_o$. These data for several different compositions are plotted in Figure 3. The points actually do lie on a straight line.[*] Furthermore, the value of $\mathcal{C}_o$ is in general about 3 lb/ft^2 for all compositions studied, except those containing flake aluminum.

For most practical purposes the rigidity η (which has the dimensions of viscosity) may be considered as being actually the specific viscosity of the material and will be referred to as such in this report. The value of η in lb-ft-sec units may be converted to poises by multiplying by 14.88.

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[*]At very low velocities the actual curve tends to pass
 through the origin rather than to intersect the y-axis
 at a finite value. One of the curves is modified to
 show this effect.

B. Resins.

The ideal resin for a castable propellant would be a relatively low viscosity liquid (about 8000 cps) at room temperature, having a low volatile content, and preferably of density less than 1.0, so as to permit filling with a high weight percentage of $KClO_4$ while maintaining a volume percentage of about 55%. Mixtures with much higher volume percentage of $KClO_4$ do not flow sufficiently to cast properly. The resin should be sufficiently stable to permit storage and handling at room temperatures for periods of several weeks. When a small amount (e.g. 1-2%) of a catalyst is added, it should cure in 24-48 hours at a moderate temperature preferably not over 60°C. The shrinkage during cure should be as small as possible and there should be no elimination of water or other volatiles. The cured material should have rubbery properties at all temperatures so as to be able to absorb mechanical and thermal shocks without developing cracks. It must not flow at 60°C under its own weight. Furthermore, its chemical stability should be such that the physical properties do not change after long storage at 60°C.

The number of resins we have been able to locate with approximately these properties is quite small. They are listed in the following table with criticisms of their properties.

Resin	Criticism
Cordolite 708--Furfural (80-20) Cordolite 708 is a phenolic type resin derived from Cashew Shell Oil. Irvington Varnish and Insulator Co.	Liquid resin is too volatile. Cured resin hardens on continued heating.
NDRC-Westinghouse Potting Compound. Westinghouse Electric and Manufacturing Co.	Initial viscosity too low (350 cps). Cured product too hard.
CR-39 resin. Columbia Chemicals.	Initial viscosity too low. Product has low tensile strength when cured at 60°C.
Q-166 experimental resin. The Dow Chemical Co.	Liquid resin has high volatility. Shrinkage during cure too large. Final product too hard.

Styrene Base Potting Compounds
  Monsanto Chemical Co.
  Raybestos-Manhattan Co.
	Liquid resins have high volatility.

25% Solution of Rubber in Dibutyl Phthalate containing sulfur and accelerators.	Is essentially a gel at room temperature. Must be handled at 60°C. Must be cured at 100°C.
Paraplex P-10. Resinous Products and Chemical Co.	Liquid resin has too high volatile content.
ZV5273 resin. A modified 2851 Permafil. General Electric Co.	Cured resin lacking in tensile strength. Tendency to be crumbly.
2851 Permafil. General Electric Co.	Cured resin lacking in tensile and tear strength.
Thiokel LP-2. Thiokol Corp.	Question of stability in presence of $KClO_4$ would have required extensive investigation. Combustion products extremely malodorous.
BRS 16631. Bakelite Corp.	Initial viscosity too low. Liquid resin too volatile. Cured product too hard.

Many of the resins listed here were suggested by Mr. M. M. Safford, consultant to Division 8, NDRC, and Mr. M. C. Agens, both of the General Electric Co. Their active interest in this work has been very helpful and is hereby acknowledged.

Several further possibilities existed in the use of solutions of certain synthetic elastomers in non-volatile plasticizers, for example, Neoprene KNR dissolved in dibutyl sebacate to form a solution of the required viscosity. These were not investigated due to the practical difficulty in making such solutions. The plasticizers are generally not active solvents and therefore solution is very slow. Moreover, the elastomers are usually supplied in large pieces which must be cut up before dissolving.

A series of materials marketed by the Bakelite Corporation under the class name of Plastisols were considered. These are suspensions of finely divided synthetic resins, usually Vinylites, in plasticizers which are inert at room temperature.

When the temperature is raised sufficiently, however, diffusion of the plasticizer into the resin occurs, and a gel of rubbery characteristics is obtained. We learned indirectly that experimental work with this type of material was being pursued by Aerojet Engineering Corp. and so made no further investigation of them.

ZV5273 resin of the General Electric Co. was selected as being probably the most suitable of the available resins. Its composition is

> 33.4 parts Oleic Acid
> 58.8 parts 2851 Permafil
> 6.5 parts Butyl Methacrylate monomer
> 1.3 parts t-Butyl perbenzoate

Its properties closely approximate those of the ideal resin, lacking only, insofar as we were able to tell initially, a high tensile strength. This should be of little consequence, since during firing the propellant must withstand essentially compressive stresses.

The composition initially studied was

> 25% ZV5273
> 5% Al Flake
> 70% $KClO_4$

The aluminum was included because it was thought from previous work with thermoplastic compositions that it brought about a substantial reduction in the burning law exponent n . The mixing and casting procedures will be discussed in detail in subsequent sections of this report.

The extreme progressive burning previously discussed was encountered immediately on test firing this composition and experiments were initiated to determine the cause of the formation of cone-shaped surfaces. Pertinent data on the cause of cone formation are summarized in the following table.

	Grain Axis	Grain Periphery
*Rate of Burning at 1215 psi	0.92 ± 0.01	0.98 ± 0.02
*Rate of Burning at 720 psi	0.63 ± 0.03	0.68 ± 0.02
+Heats of Reaction cal/gm	906 ± 11	932 ± 9
Density gm/cc	1.779 ± 0.004	1.785 ± 0.002

*Strands cut parallel to axis and burned in Crawford bomb.
+At 75°F in 20 atm of nitrogen.

These data indicated strongly that a difference in composition existed between the grain periphery and the axis. It was not possible to calculate, however, whether the observed difference in burning rates would account for the cone formation since the exact radial distribution of rates was not known. The difference in density of 0.006 corresponded to a difference of 0.29% in $KClO_4$ concentration, which in turn corresponded to a difference of 5.7% in burning rate between the grain axis and periphery. This checked closely with observed differences of 6.3-7.6% from the above table.

Other experiments were performed to test various possible mechanisms which might produce more rapid burning at the periphery of the grain. X-ray photographs of the grains showed the distribution of air bubbles to be completely random, eliminating the possibility that they might cause the cone-shaped surface. Grains were made up in which the filler was 1:1 $KClO_4$-$Ba(NO_3)_2$, the $KClO_4$ (Sp.Gr.2.52) being all of a large particle size and the $Ba(NO_3)_2$ (Sp.Gr. 3.24) being all of a small particle size. X-ray photographs of these grains failed to show any gradation in photographic density as would have been the case had any preferential distribution due to particle size occurred. Concurrent experiments with restrictive coatings of various types and thicknesses eliminated the possibility that heat transfer into the grain during burning was the essential cause of cone formation. Orientation of Al flake was shown not to be a factor since grains differing only in that the Al flake was replaced by an equal weight of $KClO_4$ still showed coning.

The hypothesis was advanced that during the curing process some change in composition may occur as a result of the fact that heat is transferred from the outside inward and that the center of the grain therefore reaches curing temperature considerably more slowly than the outside. The oleic acid in ZV5273 resin almost certainly does not enter the polymerization reaction and could conceivably migrate from one portion of the grain to another, although it is difficult to visualize a mechanism which would bring about such migration.

Experiments to check the validity of this hypothesis are summarized in Table I. The values reported are the average of several measurements, usually eight. While there were indications that less surface change would result from curing two weeks or longer at 60°C, thereby presumably allowing equilibration of oleic acid, such a procedure was considered undesirable from the standpoint of manufacture. Moreover, the possibility existed that the oleic acid could migrate on long storage into restrictive coatings and cause failures. Accordingly, a number of variations in the resin composition

were tested. These variations are included in Table I, which shows a marked trend toward less surface change the fewer the components of the resin. The increasing viscosity appears to be only coincidental. As a result of these experiments, a resin consisting of

> 98.7 parts 2851 Permafil
> 1.3 parts t-Butyl perbenzoate

was chosen for further development. The t-Butyl perbenzoate serves as a catalyst for the curing reaction. 2851 Permafil, obtained from the General Electric Co., is a reddish, slightly fluorescent liquid having a viscosity of about 8200 cps at 25°C depending somewhat on the age of the sample. Its density is 0.98 gm/cc at 25°C. The resin has a shelf life of several months when stored at room temperature. This can be extended considerably by bubbling air through the resin, oxygen being an effective inhibitor for further polymerization. Other inhibitors are quinone, hydroquinone, and t-butyl catechol when used in amounts of 0.02%. The volatile content is practically nil.

Various organic peroxides may be used to catalyze the cure, t-butyl perbenzoate* being chosen because it is a liquid of low volatility which dissolves readily in 2851 Permafil. After addition of t-butyl perbenzoate, the resin has a life of 8-20 hours at room temperature. At 60°C it gels rapidly and cures in 20-24 hours. The solid resin has a density of 1.00 gm/cc at 25°C, the shrinkage during cure therefore being quite small. The surfaces exposed to air usually remain soft and sticky due to inhibition by oxygen, but this may be remedied, if desired, by covering the surface with cellophane.

The cured resin is a rubbery solid, insoluble in any of the common organic solvents and in water. It may be dissolved with decomposition in boiling concentrated caustic solution. The resin shows no flow at 60°C under its own weight, either filled or unfilled. At -40°C the resin is no longer rubbery, but when dented by the fingernail slowly returns to the original shape. It is non-brittle at -40°C, samples having been dropped from a height of several feet on concrete without fracture. It has a low tensile strength and little tear resistance.

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*Union Bay State Chemical Co., Peroxide Division, Cambridge, Mass.

TABLE I

Effect of Cure Conditions and Resin Composition on Increase of Burning Surface.

All tests with 4" diameter, 8" long grains.

Resin Composition	Resin Viscosity (cps)	A_f/A_i*	h_c-h_o, in.+	Remarks
33.4 pts. Oleic Acid 58.8 pts. 2851 Permafil 1.3 pts. t-Butyl perbenzoate 6.5 pts. Butyl methacrylate	600	1.182	1.23	Cure: 2 days at R.T. plus 20 hrs. at 60°C.
"		1.226	1.08	Cure: 5 days at R.T. plus 20 hrs. at 60°C.
"		1.194	1.28	Cure: 7 days at 60°C.
"		1.083	0.75	Cure: 14 days at 60°C.
33.4 pts. Oleic Acid-Ethocel(80-20) 58.8 pts. 2851 Permafil 1.3 pts. t-Butyl perbenzoate 6.5 pts. Butyl methacrylate	6800	1.149	0.99	Cure: 20 hrs. at 60°C.
92.2 pts. 2851 Permafil 1.3 pts. t-Butyl perbenzoate 6.5 pts. Butyl methacrylate	5400	1.120	0.71	Cure: 20 hrs. at 60°C.
83.7 pts. 2857 Permafil 1.3 pts. t-Butyl perbenzoate 15.0 pts. Butyl methacrylate	5500	1.076	0.50	Cure: 20 hrs. at 60°C.
98.7 pts. 2851 Permafil 1.3 pts. t-Butyl perbenzoate	8200	1.065	0.43	Cure: 20 hrs. at 60°C.

*A_f/A_i is the ratio of final burning surface to initial burning surface neglecting the contribution of "pitting".

+h_c-h_o is the elevation of the highest point of the grain surface above the periphery.

C. Other Composition Variables.

   1. Influence of Composition on Behavior During Burning.

The very large progression which occurred when test firing
was started on grains of the composition

           25% ZV5273
            5% Al flake
           70% $KClO_4$

has been discussed in a previous section of this report, and
shown to result from two phenomena. One is an increase in
the apparent area by formation of a projecting cone; the
other is a small scale surface increase called pitting.
Experiments which led to substantial elimination of cone
formation have been discussed previously.

There is one other possible reason for progression in excess
of that due to increase in apparent area; some effect may
exist (e.g. radiation effects) which depends on the amount
of free space in the motor, influencing behavior more as the
grain is consumed and the free space increased.

Table II contains data from experiments relating composition
to progression. It is seen that the amount of progression
in excess of the surface change is decreased by increasing
the free space in the case of aluminum compositions. If a
grain of this composition is partially burned, then replaced
in the same test motor and re-ignited, the grain begins to
burn the second time at the pressure at which it was burning
when interrupted. The effect, whatever it may be, appears,
therefore, to be permanent; but a rather obvious experiment,
that of re-igniting a partially burned grain in a motor having
an amount of free space equal to the amount at the beginning
of the first firing, has not been done.

This effect is, from Table II, not as marked in compositions
which do not contain aluminum, although no direct experiments
have been made with these compositions on the effect of free
space. Since the aluminum has been shown to serve no good
purpose otherwise, contrary to earlier experience with thermo-
plastic propellants (Appendix A), a very considerable decrease
in progression was obtained by its omission.

There remains, however, some progression in excess of that due
to surface change with aluminum-free compositions. This is
probably due to a semi-microscopic surface change, resulting
possibly from incomplete dispersion of $KClO_4$.

Table II

Influence of Composition on Progression of Pressure

Composition	$(P_f/P_i)/(A_f/A_i)^{\frac{1}{1-n}}$	Remarks
25% ZV 5273 5% Al flake 70% KClO$_4$	2.87	Standard Test Motor
25% ZV 5273 5% Al flake 70% KClO$_4$	1.34	Fired in motor with 7" of free space between grain and nozzle.
25% (92.2% 2851 Permafil (1.3% t-Butyl perbenzoate (6.5% Butyl methacrylate 0.5% Carbon 74.5% KClO$_4$	1.51	Standard Test Motor.
25% (98.7% 2851 Permafil (1.3% t-Butyl perbenzoate 0.5% Carbon 74.5% KClO$_4$	1.34	Standard Test Motor
25% (98.7% 2851 Permafil (1.3% t-Butyl perbenzoate 75% KClO$_4$	1.30	Standard Test Motor

Carbon seems to have little effect on the progression in excess of that due to surface change. The surface change, however, was decreased from 7.9% to 4.1% in one series of experiments by addition of 0.5% of Excello carbon black.

2. Effect of Al flake and Other Additives on n and Rate of Burning.

From previous work with cast perchlorate propellants based on a thermoplastic resin (See Appendix A), it was thought that addition of about 5% of Al flake would cause a substantial reduction of the burning law exponent $\underline{n}$ in the case of thermosetting compositions. Data from the Crawford burning rate bomb relative to Al flake and other additives are summarized in Table III. The precision of this method for measuring $\underline{n}$ is reflected in an average deviation of 0.02, or 2.95%, and a maximum deviation of 5.90%, in a series of ten measurements. The precision of the burning rate measurement has been 4.7%. Inspection of Table III shows that no significant reduction of $\underline{n}$ resulted from addition of Al flake, Ammonium Picrate, Ammonium Nitrate, or Carbon in amounts from 2 - 10%. All of these except Ammonium Picrate, however, caused a definite decrease in the rate of burning. No experiments of this sort were done with 2851 Permafil propellants, inasmuch as it seemed unlikely that there was enough difference chemically to cause results differing from those with ZV 5273, and increased rates of burning were desired rather than decreased.

Table III

Effect of Al flake and other additives on $\underline{n}$ and rate of burning of ZV 5273 - $KClO_4$ propellants

Composition	R_{1000}	n	S_W
25% ZV 5273 75% $KClO_4$	0.93 0.93	0.73 0.65	1170 650
25% ZV 5273 5% Al flake 70% $KClO_4$	0.85 0.78	0.68 0.64	1100 650
25% ZV 5273 10% Al flake 65% $KClO_4$	0.73	0.66	500
25% ZV 5273 5% NH_4pic. 70% $KClO_4$	0.89	0.77	1170
25% ZV 5273 10% NH_4pic. 65% $KClO_4$	0.91	0.75	1170
25% ZV 5273 5% NH_4NO_3 70% $KClO_4$	0.94	0.72	1370
25% ZV 5273 10% NH_4NO_3 65% $KClO_4$	0.84	0.78	1370
23% ZV 5273 2% Carbon 75% $KClO_4$	0.83	0.65	1400

3. Effect of $KClO_4$ concentration and particle size on rate of burning and exponent n

The variation in rate of burning with $KClO_4$ concentration and its specific surface (S_w) in square centimeters per gram is shown in Figures 4 and 5 for the two propellants which we have investigated. These data were obtained from the Crawford burning rate bomb.

The lack of dependence of rate of burning on $KClO_4$ particle size in the case of the propellant using 2851 Permafil as a matrix is a pleasant state of affairs from the point of view of process control. However, it leaves an increase in $KClO_4$ content or omission of carbon as the only means of obtaining a higher burning rate. Time did not permit a complete investigation of these possibilities. However, we estimate 80% of $KClO_4$ as the maximum consistent with ease of casting, and from extrapolation of the data of Figure 5, 0.90 in/sec at 1000 psi as the maximum rate of burning.

The following table shows the effect of $KClO_4$ concentration on the exponent n for the ZV 5273 propellant.

% $KClO_4$	n
65	0.71 ± 0.01
70	0.68 ± 0.02
75	0.65 ± 0.02

The data reported are averages of five to eight determinations. There appears to be a slight but significant trend toward lower exponent the more $KClO_4$ present.

The effect of $KClO_4$ particle size on n in the ZV 5273 propellant may be seen from the following:

S_w Range	n
500 - 900	0.66 ± 0.03
1100 - 1500	0.69 ± 0.03
1700 - 2200	0.71 ± 0.02

The values reported are again averages of several determinations. While there seems to be a trend toward higher exponent as the particle size decreases, the change is so small as to be hardly significant.

4. Effect of Composition on Specific Impulse.

It is of considerable interest to know the way in which the specific impulse varies with the $KClO_4$ concentration in the range which is practical for a castable propellant (70-80%). Further, there were possibilities both of lowering the flame temperature and of increasing the specific impulse by substitution of NH_4NO_3 for a part of the $KClO_4$. These points have been investigated using 1 inch diameter perforated grains and restricted so as to be neutral burning. Measurements were made on the pinwheel apparatus* at 1000 psi and unit nozzle expansion ratio. Data are summarized in the following table and in Figure 6.

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* OSRD Report Nos. 857 and 1627.

Composition	I (sec) at 1000 psi and Unit Expansion
30% { 98.7% 2851 Permafil { 1.3% t-Butyl perbenzoate 0.5% Carbon 69.5% KClO$_4$	119 ± 0.3
25% { 98.7% 2851 Permafil { 1.3% t-Butyl perbenzoate 0.5% Carbon 74.5% KClO$_4$	128 ± 1
21% { 98.7% 2851 Permafil { 1.3% t-Butyl perbenzoate 0.5% Carbon 78.5% KClO$_4$	132, 137 ± 1
19.5% { 98.7% 2851 Permafil { 1.3% t-Butyl perbenzoate 0.5% Carbon 80% KClO$_4$	136 ± 2
25% { 98.7% 2851 Permafil { 1.3% t-Butyl perbenzoate 0.5% Carbon 10% NH$_4$NO$_3$ 64.5% KClO$_4$	128 ± 1

When the expansion ratio was 7, the second composition was
found to have a specific impulse of 159 ± 3. In line with
previous experience an additional increase of 5-10% would be
expected with large grains as compared to 1" diameter grains
due to differences in heat losses.

There appears to be no gain in specific impulse on substitution
of NH$_4$NO$_3$ for KClO$_4$, but the decrease in flame temperature
might well be advantageous.

5. Factors influencing the flow properties of the uncured propellant

The flow properties of the uncured fuel are of interest in so
far as they govern the way in which the material may be handled
during the operations of mixing and casting.

Referring to Section IIA-3, the terms T_o and η are used to describe the flow properties of a typical cast perchlorate propellant. Although no definite optimum values may be established for T_o and η, a few qualitative statements can be made. The value of the yield strength, T_o, should be sufficiently small that any entrapped bubbles will be able to rise easily to the surface, and still it should have a finite value so that settling is avoided. The "viscosity", η, should be low enough that the fuel is readily pourable, and entrapped bubbles can be readily disengaged, but should not be so low that settling can occur. The values of T_o and η for the fuel finally adopted as standard are probably of the right order of magnitude.

The effects of several variables upon the flow properties have been investigated; the results are described below.

Effect of Particle Size

The effect of particle size on the viscosity of the "standard" composition is shown in Figure 8. The reason for the decrease in viscosity with decreasing particle size has not been definitely established. It may be that a greater range of particle sizes is produced as finer grinds are made. This permits the voids among the largest particles, which in coarse grinds are occupied largely by liquid, to be partially filled with fines; accordingly, some of the binder is displaced and the fluid films between the large particles are thereby thickened, thus decreasing the overall viscosity. This is the familiar close-packing effect.

Effect of Solids Content

The variation of viscosity with the percentage by weight of solids is shown in Figure 7. The sharp rise is possibly representative of a critical solids-liquid ratio at which the particles actually touch one another, and solid-solid friction is experienced in addition to the normal fluid-film friction.

Effect of Wetting Agent

The following table illustrates the effect upon the viscosity of the "standard" composition of the addition of 0.5% of lecithin to the binder.

Specific surface of $KClO_4$	Viscosity (Poises) with lecithin	without lecithin
600	4030	6100
1800	2320	4560

This wetting agent has a very real effect, perhaps acting by causing the breakdown of aggregates, thereby effecting better dispersion.

Effect of Aluminum

The effect of flake aluminum upon the viscosity is shown by the following table:

Composition % by weight	Percentage by volume of binder	Yield Strength lb/ft^2	Viscosity Poises
25% Binder (98.2% Permafil / 1.3% EP4 / 0.5% Lecithin) 0.5% Carbon 74.5% KClO$_4$ S$_W$ = 1200	45.6	3.0	3040
25% Binder (98.2% Permafil / 1.3% EP4 / 0.5% Lecithin) 5.0% Aluminum flake 70.0% KClO$_4$ S$_W$ = 1200	45.8	6.0	4300

Although the substitution of the denser aluminum for part of the perchlorate causes a slight increase in the percentage by volume of binder, there is a distinct rise in both the viscosity and yield strength. This effect is due to the leaflike character of the individual particles of aluminum which gives rise to interlocking, and obstruction of flow between the perchlorate grains.

Effect of viscosity of binder

No systematic study was made of the effect of variations of the viscosity of the binder; however, one batch made up with a very fluid binder, and containing 81.5 per cent by weight of perchlorate was about as pourable as the standard composition with 75% solids and viscous Permafil binder.

D. Mixing Procedures

Practically all of the experimental work on mixing has been done with a machine of kneader or dough mixer type equipped with Sigma blades. This type of machine would seem to be ideal for this work since it provides the high shearing forces and the kneading and folding action necessary for complete dispersion of the solid particles in a viscous binder, and for thorough blending of the batch. Furthermore, it is readily adaptable to vacuum operation, heating or cooling of the batch, and to the casting operation.

Most of the work was done with a 2 gallon capacity Baker-Perkins machine, but more recently a Read machine of 5 gallon capacity has been acquired. Both machines are jacketed for circulation of a cooling or heating medium and both are fitted with vacuum lids through which vacuum and pressure connections are made. An opening is provided in the cover for discharge of the batch by tilting the mixing bowl. During the mixing operation the lid may be held in place by lugs provided or by the internal vacuum alone. The latter is preferable since it would reduce the violence in case of accidental ignition of the batch. The Read machine is fitted with a hopper from which the $KClO_4$ may be fed under vacuum and with openings for charging liquid ingredients.

The original procedure used was to charge the liquid resin, including catalyst, then to add the solid materials as rapidly as they could be folded in. The lid was put in place and the mixing bowl evacuated to 12 to 20 mm. absolute pressure. Mixing was then continued for one hour. The vacuum was used to prevent mixing in of air which would lower the density of the propellant and which might affect adversely the ballistic properties.

Batches were frequently found to have "set up" in the mixer to the point that they could not be cast because of heating from the mixing action. The resin cure is exothermic and consequently relatively little heating from the mixing action will initiate a process which is self-maintaining, the cure reaction increasing the temperature and viscosity and the increased viscosity in turn causing still greater heating due to mixing. Temperatures inside the batch occasionally were as high as 50°C. Two steps were taken to prevent setting up from occurring: (1) Cooling water was circulated in the jacket. The maximum water temperatures were 21-22°C. (2) Instead of adding the catalyst at the beginning of mixing 0.02% of quinone, based on the amount of resin, was added to serve as an inhibitor for the cure reaction and mixing carried out as usual. The catalyst was then added

after 50 minutes mixing and mixed in during the last 10 minutes.
The maximum batch temperature attained since adopting this
procedure has been 32°C, and no further difficulty with pre-
mature set-up of the batch has occurred.

Because one of the resins used in the early work, ZV 5273, con-
tained an appreciable amount of volatile material it was found
necessary to place a trap containing activated carbon in the
line between the mixer and the vacuum pump to prevent contamina-
tion of the oil by materials which might polymerize in the moving
parts.

After the above mentioned effects of formation of a conically
shaped burning surface and of progression far in excess of
that attributable to the change in burning surface had been
eliminated by changing the composition, there still remained
a general roughening and cratering of the burning surfaces
such as may be seen in Plate 1. This was thought to arise
from air bubbles or actual inhomogeneities in the batch and
some experiments were done to find the effect of batch size,
mixing time, and mixing procedure on progression. Unfortunately,
no clearcut conclusions could be drawn from these because
batchmaking capacity was limited and it was not possible to
test fire the large numbers of grains necessary to demonstrate
any improvement. Furthermore, no method was available for
measuring areas of irregular surfaces, so that little more
than a feeling of relative quality could be obtained.

The following mixing procedure, consisting of two distinct
stages, has been adopted as probably approaching the optimum
for this type of mixer.

1. Forty percent of the total amount of resin to be used in the
batch is charged into the mixer along with all of the carbon and
quinone and mixed for 3-5 minutes to insure wetting of the
carbon. All of the potassium perchlorate is then added as
rapidly as it can be folded in. The cover is then put in place,
the vacuum applied, and mixing continued for one-half hour.

When the perchlorate is first added, the mixture appears very
dry and crumbly, but as mixing proceeds the mass becomes doughy
and at the end of thirty minutes has the consistency of a putty.
This stage affords opportunity for the breakdown of agglomerates
and wetting of individual particles because of the relatively
high shear stresses.

2. At the end of one-half hour the remainder of the binder is
added and mixing is continued for 20 minutes. The catalyst is

then added and the batch mixed an additional 10 minutes. During this stage the perchlorate becomes dispersed evenly throughout the resin and forms a viscous but fluid suspension.

Cooling water is circulated in the jacket throughout the entire process. The appearance of the batch just after adding perchlorate, at the end of one-half hour, and the finished batch may be seen in Plates 2, 3, 4 and 5, as well as a view of the interior of the mixing bowl.

E. Casting

1. Molds

The molds used have been of two types which are sketched in
Figures 9 and 10. The one consists of a length of Shelby
tubing on one end of which is threaded a steel cap. Before
use this mold must be lined with some material which will
prevent sticking of the propellant to steel and which will
allow the cured grain to be easily pushed out. Heavy kraft
paper or varnished cambric have been used. Either of these
can readily be stripped off the grain and leave smooth uniform
surfaces.

The split mold must be coated with a separating compound to
prevent the propellant from sticking to the steel after cure.
A mixture of soap and glycerin in the ratio 1:4 has been
successfully used.

These molds may be readily adapted for molding perforated
grains as shown in Figure 11. The mandrel may be wrapped with
collophane or coated with soap-glycerin mixture.

2. Casting technique

Considerable air can be trapped in the grains during casting
unless suitable techniques are used. Two schemes have been used
successfully.

In the first scheme, a 1-1/4 inch pipe of length slightly greater
than the height of the mold is attached to the plug valve set
in the discharge opening of the mixer. The mold is raised about
this pipe until the end of the pipe is about 1/2 inch above the
bottom of the mold. The fuel is then allowed to flow from the
mixer through the pipe under an air pressure of 10 psi, applied
through connections in the mixer lid. When the liquid propellant
has risen in the mold to about 1/2 inch above the end of the
pipe, the mold is slowly lowered so that the end of the pipe
remains at a constant distance below the surface of the fuel.
Apparently satisfactory results have been obtained using this
method, but difficulties have arisen in handling long heavy
grains. Plate 6 shows the mixer in the discharge position with
the casting pipe attached.

The second scheme consists in placing the mold in a closed chamber

which can be evacuated to a very low pressure. The propellant is allowed to flow through a pipe set in the top of the vessel and falls into the mold. Any air bubbles present become greatly expanded and break, and the mold is thus filled with a completely de-aeroated product. Plate 7 is a photograph of a vacuum casting chamber of suitable design.

We have not been successful in demonstrating experimentally any superiority of either casting method. Use of the vacuum casting technique does give charges more free from air, however, and is probably to be preferred.

F. Curing

During the curing operation the liquid propellant is converted to a resilient solid by reason of a chemical reaction resulting in cross-linking of the resin. This cross-linking reaction is an exothermic one and may conceivably result in the temperature at the center of a large mass of propellant becoming quite high or possibly in ignition.

Several experiments were made using 8.5" x 8" solid cylinders in which the temperature at the center of the grain was measured by means of a thermocouple while the grain was curing in an oven at 60°C. Seven to eight hours were required for the grain center to reach oven temperature, while the maximum temperature ever attained was 63°C.

We have used consistently a cure of 24 hours at 60°C. for 4" diameter grains and 48 hours at 60°C. for 8.5" diameter grains. Very few experiments have been made on varying cure conditions and these failed to show any appreciable effect.

G. Restrictive Coatings

The restrictive coatings developed at this laboratory for use with composite propellants consist of two parts, a primary coating of paint or similar substance applied to the surfaces to be restricted, and a gross protective coating of industrial tape whose function is to insulate the primary coating so that it will not be burned through by hot gases. The requirements are that the primary coat adhere to the grain surfaces at least as strongly as the cohesion of the grain itself, and further that the gross protective coating adhere to the primary coating sufficiently strongly that it not be separated by rough handling, temperature cycling, or any other treatment which might be encountered during shipping, handling, or use.

Initial work with restrictive coatings for cast perchlorate propellants was toward development of a coating of this type. A number of coating materials were tried and several, including Melmac 599-8, Harvel 1301, G.E. 1170, Paraplex AL-16, Sterling S-142, and G.E. 1201, selected for further trial. It was found that, while these materials adhered well to the grain surfaces, removal of the tape removed the coating, bringing a thin layer of the grain surface with it. Nonetheless, they were satisfactory for shots at ambient temperatures and two sprayed coats of Paraplex AL-16 plus four layers of Jonflex tape, has been used extensively for test firing. Forty charges 8.5" diameter have been so coated and fired without failure. 300 charges 4" diameter so coated have been fired at ambient temperatures with at most five failures which can be attributed to the coating. However, at -40°C these coatings were not satisfactory. Frequently spaces developed between the grain and tape, due to differences in the thermal coefficients of expansion and to poor adhesion, leaving the grain unprotected.

Attention was turned briefly to the possibility of potting cast grains. Here the grain would be centered in a loosely fitting container, or a rocket motor, and the space between the grain and the wall filled with a liquid resin which could be cured at mild temperatures to a rubbery solid which would bond well to both the grain and the wall. Mandrel wrapped cellulose acetate tubes and paper tubes proved to be unsatisfactory since they deform easily, causing the potting material to pull away from the charge. A number of failures were the result of potting directly into motors using G.E. 2851 Permafil or 2851 Permafil Q 166 (1:1). This method of restriction was not pursued further.

Another coating scheme which was found to be satisfactory with composite propellants seemed to be the ideal coating for use

with cast perchlorate propellants. The scheme as previously used called for two coats of Paraplex AL-16 on the grain, a similarly coated disc of 1155 (high density) cork on the bottom end, and a 7.9" diameter mandrel wrapped rubber tube stretched over the coated cylindrical surfaces. The rubber tube is quickly and easily applied as follows: the rubber tube is placed inside a steel tube of larger diameter and shorter length. The ends of the rubber tube are stretched over the steel and turned back over the outside, and the space between the rubber and steel evacuated, stretching the rubber against the steel. The whole is then placed over a coated grain and the vacuum released allowing the rubber tube to shrink on to the grain. After warming for two hours at 60°C. to allow the tube to relax, the rubber is trimmed flush with the grain ends.

Of 13 shots fired with this coating, 3 were failures attributable to the coating. No explanation for these failures was apparent, but the hypothesis that pressure differentials existing momentarily in the motor caused the tube to bulge so that burning could flash down the side seemed reasonable. Two changes were made in the coating: the primary coating was changed to 50-50 Paraplex AP-11 - Dibutyl sebacate, a synthetic elastomeric composition which is cured 24 hours at 60°C and which adheres more strongly to both the grain and the rubber tube. Strips of cork were cemented on the outside of the rubber tube parallel to the grain axis so as to make the grain fit snugly in the test motor.

The record with this modified coating has been as follows:

Prefiring Treatment	No. Shots	Satis- factory	Failures	Type of failure
Ambient Temperature	9	7	2	One unexplained. One due to burning through bottom corner.
Fired at 60°C	6	5	1	Burned through bottom corner.
Fired at -40°C.	9	7	2	" "
Stored 60°C 1 week Fired at ambient temperature	4	3	1	" "
Stored 60°C 2 weeks Fired at ambient temperature	4	3	1	" "
Cycled 7 times. Fired at 60°C.	2	2	0	

The failures are seen to be almost all of one type, resulting from penetration of the joint between rubber tube and cork disc at the bottom corner of the grain. Moreover, all occurred at the highest values of restriction ratio used. The cork discs used had to be manually trimmed to fit and may not have been perfect in many cases, a plausible explanation for the failures.

A further modification of this coating has more recently been made. After the rubber tube has been applied as above, two layers of industrial tape are placed over the bottom and allowed to extend over the cylindrical surfaces for a distance of one inch. The tape is rolled down tightly over the bottom surface, crimped and rolled down on the cylindrical surface and finally a strip of 1" wide tape is wrapped around at the bottom of the cylindrical surface to hold the crimped tape flat. Only six test shots with this further modification were fired, all at ambient temperature, and all were successful.

While further development and more extensive testing are needed, it seems safe to conclude that the rubber tube coating can be made satisfactory. Use of a less highly plasticized Paraplex AP-11 might be advantageous, while certainly every precaution must be taken that the cork discs fit well.

H. Compensation of Progressive Burning by Grain Design

The suggestion has been made that the progressive burning which is invariably experienced with the cast perchlorate propellants investigated might be neutralized by shaping the grain so that its area would decrease throughout burning.

Actually any end-burning cylindrical grain having a non-planar initial surface will regress as burning takes place. However, it may be shown that the mode of regression, that is the rate of decrease of area as a function of the distance burned, is dependent on the initial shape of the grain. Examination of pressure-time traces obtained from uncompensated grains shows that the rate of pressure build-up is greatest at the start of burning; accordingly for perfect compensation the rate of decrease of burning area should be greatest at the beginning. Of the simple geometrical shapes considered, the projecting cone, and reentrant hemisphere give this type of regression, whereas the reentrant cone shows a rate of regression which is small at first, but increases and passes through a maximum after burning has occurred for a considerable time. The projecting cone was chosen for these experiments since it is most easily made, and calculations are simple.

The shaped grains are produced by placing in the bottom of the mold a reentrant conical former, turned from solid steel. The conical surface is covered with varnished cloth, to prevent adhesion, and the grain is cast, cured and restricted in the usual manner.

The pressure attained in a rocket motor is given by the expression

$$P = \left(\frac{A_g \, \rho \, b}{A_t \, C_D} \right)^{\frac{1}{1-n}}$$

where:

A_g = burning area of grain

A_t = nozzle throat area

ρ = density of powder

b and n are constants in the burning rate equation:

$$x = bP^n$$

C_D = discharge coefficient

Taking the ratio of pressures at the final and initial stages of burning we obtain:

$$\frac{P_{(final)}}{P_{(initial)}} = \left(\frac{A_{g(final)}}{A_{g(initial)}}\right)^{\frac{1}{1-n}}$$

A plot of $\frac{P_{(final)}}{P_{(initial)}}$ against $\frac{A_{(final)}}{A_{(initial)}}$ on logarithmic coordinates should be a straight line having a slope of $\frac{1}{1-n}$ and passing through the point (1,1).

Table IV

Compensation of progression by grain design. All grains are 3-7/8" dia. by 6-8" long.

Initial Configuration	A_f/A_i	P_f/P_i	P_{max}* psi
Flat	1	1.844	1565
Flat	1	1.484	1220
Flat	1	1.887	1626
Flat	1	2.180	
Flat	1	1.460	
Flat	1	1.498	
25° cone	0.905	0.942	942
25° cone	0.905	1.140	980
30° cone	0.865	1.009	995
30° cone	0.865	0.805	902
40° cone-truncated 2-1/2" flat end	0.850	1.499	
	0.850	1.299	
50° cone-truncated 2-1/2" flat end	0.758	0.779	960
	0.758	0.836	1014
40° cone	0.765	0.413	
40° cone	0.765	0.590	
50° cone	0.643	0.315	

*Note: grains for which pressures are given are all from the same batch and were all fired at 0.285" dia. nozzle.

Several grains terminated by projecting cone of various angles were fired, along with several flat-ended control grains. The data for these experiments appear in Table IV**, and a logarithmic plot of the pressure ratio against the area ratio is shown in Figure 12. A line of the theoretical slope (n = 0.70; slope = 3.33) is drawn so as best to represent the data. This line does not pass through the point (1,1) but rather indicates that neutral burning occurs when $A_{final}/A_{initial}$ equals 0.87,

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** A_{final} has been assumed to be equal to the cross-sectional area of the grain. Actually the initial non-planarity has not completely vanished, but the assumption is nearly correct and is made for the sake of convenience.

which corresponds to a cone of 29°, which has an area of 1.15
times that of a flat-ended grain. This is interpreted as
meaning that the roughness, which develops as an initially
flat grain burns, at the end of about 6 or 7 inches of burning
has increased the effective burning surface by 15 per cent.
Accordingly, a grain having an initial surface 15 per cent greater
than the cross-sectional area should burn neutrally. Several
pressure-time traces of compensated and uncompensated grains
are shown in Plate 9.

Table IV gives, in addition to the pressure and area ratios,
the maximum pressure attained during the burning of the grain
(neglecting the initial primer peak). The average maximum
pressure for the three uncompensated grains is 1470 ± 187 psi,
while for six grains burned at the same restriction ratio and
having an average P_f/P_i of 0.918 ± 0.112, the average maximum
pressure is 965 ± 31 psi.

If in effecting neutralization of the burning pressure we
have given the grain initially the same area which a flat-ended
grain develops only after several seconds of burning, we should
expect the initial pressure of the compensated grain to be the
same as the final pressure of the uncompensated grain, since
in both cases the same restriction ratio (A_g/A_t) prevails.
Actually the maximum pressure is nearer the average initial
pressure of the uncompensated grains, which is 845 ± 15 psi.
Apparently in the act of increasing the burning surface we
have done something which prevents the increase of pressure
normally experienced.

No explanation of this highly anomalous behavior is apparent;
however, a possible clue may lie in a phenomenon which has been
observed but never studied in a systematic way.

Some evidence exists that the large-scale pitting and cratering,
so commonly observed when flat-ended grains are burned, does
not occur when the configuration is such that the gas flow is
not normal to the surface. The surfaces of partially burned
cylindrically-perforated grains, in which the gas flow is
almost parallel to the surface, may show evidence of occasional
bubbles, and an almost microscopic roughness, but large
irregularities are absent. The pitting and cratering of
partially-burned grains was not noted with early compositions,
which gave sharply-pointed conical surfaces, but slowly appeared
as the composition was changed so as to reduce the cone angle.
A grain of somewhat different composition than usual, but
which normally does not develop conical surfaces, was cast into
a plastic cup. The restriction was faulty, permitting the
burning at the periphery of the grain to be uniformly faster
than at the center. Accordingly, a conical surface was developed,

and failure of the motor quickly occurred, because of the excessive pressure developed. The grain was recovered, and it was observed that the conical surface had developed only partially, yielding a truncated cone. The conical surface was very smooth and uniform, but the remnant of the initial flat surface exhibited the customary craters and pock marks.

It may be that gas flow not normal to the surface has a "polishing" effect, tending to remove any irregularities. It will be noted that in the cases in which the maximum pressure is less than what is expected, the gas flow is not normal to the initially conical surfaces. Referring to Figure 12, the plot of the pressure and area ratios, it is also noted that the truncated cones, which have a large area initially normal to the gas flow, show considerably less compensation than predicted by the theoretical equation.

III. Propellent Properties

As a result of the experimental development work on compositions described in the preceding section the following composition was selected for further work in full scale charges (8.5" diameter by 7" long).

$$25\% \left\{ \begin{array}{l} 98.7\% \;\; 2851 \;\; \text{Permafil} \\ 1.3\% \;\; \text{t-Butyl perbenzoate} \end{array} \right.$$

0.5% Carbon-Excello

74.5% $KClO_4$ $S_W = 1200$

Since this composition is at about the midpoint of the range of $KClO_4$ concentration and particle sizes considered, it seems probable that results obtained with it could be most easily applied to either higher or lower concentrations and specific surfaces. A typical screen analysis for $S_W = 1200$ is shown in Section IV.

The propellant is a black solid which is slightly rubbery at ambient and elevated temperatures. At -40°C it has lost its rubbery nature, but can still be dented by the fingernail, and is decidedly not brittle. It does not flow under its own weight at 60°C, and would be expected not to flow at higher temperatures due to the cross linked nature of the polymer.

The theoretical density of the propellant is 1.825 gms/cc. Measured densities have been 98-99% of the theoretical. The thermal coefficient of linear expansion of two other propellants of similar composition has been found to be $13\text{-}14 \times 10^{-5}$ per °C and this figure is presumed to be reasonably close to that for the composition under discussion.

At the time pilot plant design was undertaken an extended series of tests of sensitivity to impact, friction, and rifle bullet and of stability and ease of detonation was made using a propellant consisting of 25% ZV 5273, 5% Al, and 70% $KClO_4$. This composition was used because it was the most sensitive composition we anticipated making. Results are summarized in the following paragraphs.

A. Impact Sensitivity

Impact sensitivity was tested by Bruceton design No. 12, in which the sample is placed on a 3/4" square of 5/0 sandpaper, a 1.25" diameter plunger placed in contact with the sample and a 2.5 kg. weight dropped on the plunger. Drop height for 50% explosion of the cured propellant was 72 centimeters, for the uncured propellant

130 centimeters. For comparison the average 50% drop height for TNT is about 145 centimeters, that for Composition B about 70 centimeters, and that for Composite Propellant CP 492 about 70 centimeters.

B. Thermal Stability

This propellant shows practically no change when subjected to the usual 120°C. vacuum stability and the 135°C thermal stability tests. When subjected to adiabatic heating tests, a slow rate of heating was observed at high temperatures but no ignition occurred at 300°C. In one case, starting from an initial temperature of 140°C, adiabatic heating was continued for 188 minutes before ignition occurred at a temperature above 400°C.

C. Rifle Bullet Sensitivity

Charges cast and cured in 3" diameter pipe nipples were capped on both ends and used as targets for .50 caliber armor-piercing slugs at 75 foot range. There was an initial flash as the slug passed through the case, but in only one trial in ten was the propellant consumed. There was no fragmentation in any case.

D. Sensitivity to Frictional Impact

Tests with the frictional impact testing machine at Bruceton gave no reaction either at ambient temperatures or at 60°C.

E. Susceptibility to Detonation

A 90 gm Tetryl pellet was placed in contact with a charge of propellant cast and cured in a 3" diameter pipe nipple capped on both ends. A No. 8 detonator was led through a hole in one cap and placed in contact with the booster. The booster was sufficient to shatter the casing in all cases, scattering propellant about. In six out of ten trials some of the propellant burned. However, it was the judgement of those present that no detonation of propellant occurred.

F. Combustibility in Air

Neither the uncured nor the cured propellant was ignited in air by means of a match head, 30 gms of 1F black powder in a cellophane bag, or by loose 1F powder. Ignition was accomplished by means of fragments of composite propellant. Once ignited, it was quickly extinguished by a stream of water.

On the basis of these tests the propellant was listed by Safety and Security of Army Ordnance as Class IX, "loose pyrotechnic

materials before final consolidation," when in the mixers and
Class II, "thermite and similar burning compositions," when cast.

No comparable series of tests has been made on the material
without aluminum. However, it is certain that it will be no
more sensitive than the above composition, and should certainly
be no less stable.

The following summarizes briefly the properties of the propellant
as determined from test firing 8.5" x 6" end burning solid
cylinders. Some typical pressure-time traces are reproduced
in Plate 8.

n	0.71
Rate of burning, 1100 psi	0.77 in/sec
Restriction ratio, 1100 psi	187
Specific Impulse at 1100 psi and expansion ratio 5.4	172 sec.
Discharge Coefficient at 1100 psi	0.0081
Thrust coefficient at 1100 psi and expansion ratio 5.4	1.40

These values were obtained from Table V and from the graphs of
Figure 13. The amount of scattering in rate of burning and
pressure may be seen from Figure 13. Data are insufficient to
allow calculation of the temperature coefficient of pressure,
but it is estimated to be 0.6% per degree centigrade.

The number of shots which have been fired at -40°C and at +60°C
is admittedly small, but there have been no failures at either
temperature attributable to the propellant. A few grains have
also been cycled between -40°C and +60°C seven times before firing.
Several have been stored for periods of one and two weeks at 60°C
and have burned satisfactorily. There is some indication that
the progression is decreased by long storage at 60°C and this
should be investigated further.

Ignition has been accomplished by the use of a cellophane bag
containing 40 to 160 gms. of 1F black powder and an electric
match. While usually satisfactory, there have been some cases
in which the grain was not ignited, although the powder bag
burned producing an adequate pressure. This has been particularly
noticeable at -40°C and it may be necessary to devise an
ignition system which will maintain the pressure at a high value
for a longer time than will black powder.

The progression has been unpleasantly high and the reproducibility
correspondingly poor. This is due in part to a general roughening

of the burning surfaces illusted in Plate 1. The progression
is independent of both the pressure and temperature at which
the grain is fired, as far as can be seen from present data.
Its cause is not apparent but it can probably be eliminated by
further refinements in batch-making procedure.

Nozzles of solid copper, well contoured so as to reduce erosion,
have held up well under repeated test firings of eight second
duration at pressures of 1000-1500 psi.

Table V

Impulse and Related Data from 8.5" x 6" Grains of Cast Perchlorate Propellant

K	P_{av}	E.R.	I	c_D	c_F
184	1030	5.4	164	0.0083	1.36
184	1155	5.4	171	0.0082	1.40
184	1135	5.4	176	0.0081	1.43
184	1210	5.4	166	0.0081	1.35
173	1030	5.3	178	0.0079	1.41
173	945	5.3	174	0.0081	1.41
173	770	5.3	175	0.0088	1.54
195	1260	5.6	179	0.0085	1.52
195	1115	5.6	170	0.0092	1.56
195	1210	5.6	173	0.0087	1.50
195	1250	5.6	173	0.0082	1.42

IV. Tentative Process of Manufacture

The process of manufacture outlined below embodies the principles and operations believed to be the most satisfactory in producing cast propellant grains of high quality. The process as described has been operated to produce batches of 75 pounds each, which were cast into three grains each 8-1/2 inches in diameter and 6 inches long; the process should be entirely satisfactory on a much larger scale producing larger charges.

A process flow sheet is shown in Figure 14. The raw materials and operations are discussed below.

Raw Materials

Potassium Perchlorate is purchased from the Oldbury Electrochemical Works at Niagara Falls, New York in 100-pound drums. This material is a white, free-flowing, crystalline powder having the following typical screen analysis:

Screen No.	% Retained	
60	1.3	
80	3.1	Specific Surface = 350 cm^2/gm*
120	17.8	
170	36.8	
230	23.2	
325	10.6	
Pan	7.1	

*OSRD Report 5578

Tricalcium Phosphate "Conditioner grade" is purchased from the Monsanto Chemical Company of St. Louis, Mo., and is blended with the $KClO_4$ to act as a free-flow agent. This material is an extremely fine white powder.

Permafil Resin 2851 is purchased from the General Electric Company of Schenectady, New York, in 55-gallon drums. This material is a deep red (green by reflected light) liquid, the viscosity of which varies from 40 to 80 poises depending upon the age of the sample.

Carbon black "Excello grade" is purchased from the Imperial Oil and Gas Products Co. of Pittsburgh, Pa. in 12-1/2 lb. paper bags.

EP4 catalyst (tertiary butyl perbenzoate), purchased from the Union Bay State Chemical Company of Cambridge, Mass., is a light yellow mobile liquid, and is supplied in glass containers ranging up to 100 pounds in capacity.

Quinone is purchased from the Eastman Kodak Company of Rochester, New York. Quinone serves as an inhibitor, preventing premature polymerization of the resin during mixing.

Lecithin may be purchased from Hachmeister Chemical Company of Pittsburgh, Pa.

Preparation of Perchlorate*

Prior to grinding, the perchlorate is blended with 0.5% by weight of tricalcium phosphate**. This operation is carried out in a horizontal, rotating drum equipped with a series of angle-iron flights and takes about 30 minutes.

Grinding is effected in a high-speed hammermill such as the "Mikropulverizer" built by the Pulverizing Machinery Company of Chatham, New Jersey. The size of grind may be varied by changing the speed of operation and the size of screens in the mill; a given set of conditions produces a very uniform product. A typical screen analysis of the material most commonly employed is given below:

Screen No.	Per Cent Retained	
60	0.16	
80	0.26	
120	1.44	Specific surface = 1200 cm^2/gm
170	4.90	
230	8.68	
325	14.74	
Pan	69.92	

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* OSRD Report 5578
** Certain materials suitable as free flowing agents, e.g. MgO, strongly catalyze the resin polymerization and hence cannot be used.

Mixing

The sigma-blade type mixer (such as the Read machine shown in Plate 2) is believed to be best suited to this process. The machine should be equipped with a jacket through which cooling water is circulated, and a vacuum lid and stuffing boxes.

A small rotary vacuum pump serves to evacuate the mixer bowl during operation. Although it is not necessary when using straight Permafil 2851 binder, a trap containing activated carbon set in the vacuum line between the mixer and pump removes any volatile materials which may contaminate the pump oil, or polymerize in the pump.

The composition of the propellant chosen as standard is given below:

$$
25\% \text{ binder}
\begin{cases}
98.2\% \text{ Permafil 2851} \\
1.3\% \text{ EP4 catalyst} \\
0.5\% \text{ Lecithin} \\
0.03\% \text{ Quinone}
\end{cases}
$$

0.5% carbon black
74.5% potassium perchlorate

Forty per cent of the total amount of Permafil to be used is charged into the mixer, along with all of the lecithin, quinone and carbon black. The mixer is started and at the end of a minute or so, when all of the carbon has been wetted, the perchlorate is added as rapidly as it can be folded into the binder. When the addition of perchlorate is complete, the machine is stopped, the lid bolted on, and a vacuum is applied. The mixer is again started and allowed to run for one-half hour.

At the end of one half-hour the machine is stopped and the remainder of the Permafil is added. The mixer is started and allowed to run for twenty minutes more, when the EP4 catalyst is added. The mixing is continued for ten minutes longer to insure complete blending of catalyst into the batch. During this stage, and also the first, an absolute pressure of 10-15 mm. of mercury is maintained in the mixer bowl.

Preparation of Molds

Molds of the type shown in Figure 9 are lined with varnished cambric prior to use. For best results the varnished cloth is held in place with a small amount of low melting soft adhesive such as Ethocel-Castor oil (25-75). Split molds (Figure 10) are coated with a thin film of Soap-Glycerin (1:4) brushed on at about 100°C and the excess wiped off.

Casting

The cover of the mixer is bolted on and the bowl is tilted to the discharge position as shown in Plate 6. A vacuum casting chamber, as shown in Plate 7, is attached to the discharge valve of the mixer. The prepared mold is placed in the casting chamber, the door is closed and a vacuum of 10-15 mm absolute pressure is produced in the chamber. The discharge valve is then opened and the propellant flows into the mold from the mixer bowl which is at atmospheric pressure. As the propellant flows into the evacuated chamber all air bubbles are removed. When the mold is filled, the valve is closed, air is admitted to the chamber, and the full mold removed.

Curing

The molds containing the unpolymerized propellant are placed in an oven maintained at a temperature of 60-65°C. for a period of 48 hours, during which time a resilient solid forms. The molds are then removed and allowed to cool to room temperature. The grains are removed from the molds and the cloth lining peeled off. A thin layer of material which has not polymerized because of exposure to the air is then scraped from the top surface of the grain.

Restriction

The cured grain is carefully inspected for flash marks and these are removed by light sanding. If soap-glycerin mixture has been used to prevent sticking to the mold, the entire grain surface is sanded.

One end and the cylindrical surfaces of the grain are spray-coated with a solution of the following composition:

Acetone	50%
Dibutyl Sebacate*	24.75%
Paraplex AP-11*	25%
t-Butyl perbenzoate	0.25%

The t-butyl perbenzoate is added to the solution just before use. A disc of #1155 cork (Armstrong Cork Co.), 1/2 in. thickness and the same diameter as the grain, is coated on one surface at the same time. The grain and cork disc are allowed to stand

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* The Resinous Products and Chemical Co., Philadelphia, Pa.

at room temperature for at least 6 hours to allow evaporation of acetone. A second sprayed coat is applied and allowed to dry overnight.

The cork disc is placed on the coated end of the grain and rolled down using a hand roller and working from the center to the outside. This process removes air and insures good sealing.

A length of seamless smooth-surfaced rubber tube 3/32 to 1/8 inch in thickness and having an inside diameter 1/2 to 3/4 inches less than the grain diameter is placed inside a length of steel tubing about 1-1/2 inches longer than the grain and 1 inch larger in inside diameter. The ends of the rubber tube are stretched over the steel tube and turned back over the outside. The space between the rubber and steel is then evacuated and the rubber is expanded by atmospheric pressure against the inner surface of the steel tube. The whole assembly is lowered around a coated grain, the vacuum is released, and the rubber tube allowed to shrink onto the grain. The rubber tube and grain are then removed from the steel tube.

The rubber tube coated grain is placed in an oven at 60°C for 48 hours to allow the rubber to relax in the direction of the grain axis and to cure the resinous primary coating.

After cooling, the rubber tube is trimmed flush with the cork disc and to within about 1/4 inch of the other end. Two layers of industrial tape (e.g. Jonflex, Utilitape) are placed over the cork disc, lapped about one inch over the cylindrical surface, and secured by two layers of one inch width tape around the grain. Strips of cork 1/4 inch wide and the same length as the grain may be cemented to the rubber, using a rubber cement, if desired to center the grain in the motor.

A sectional drawing of the finished charge is shown in Figure 15.

V.   Recommendations for Future Work

Experimental work with the propellant described in the foregoing sections has progressed sufficiently to demonstrate that the fundamental ideas on which the work was based are sound and that the composition developed has the desired physical properties. The propellant must be made more reliable and more reproducible ballistically, however, before it can be considered entirely satisfactory. Some way must be found to reduce the progression in pressure which occurs during burning and the restrictive coating must be further improved.

The possibility of compensating for progression by grain design has been discussed previously in this report. Compensation can be easily accomplished by using a grain with a projecting cone as the initial burning surface, and would be advantageous in that such a grain would be equivalent in thrust developed to one with plane burning surface of somewhat larger diameter. Probably more desirable, however, would be to find the cause of the progression and ways of eliminating it. If the latter is to be done, some method of estimating the apparent area of irregular surfaces would be useful in that comparison of the pressure increase with area increase could then be made using an interrupter burner.

The irregular surfaces probably develop as a result of inhomogeneities in the propellant. A thorough investigation of mixing, casting, and curing procedures should reveal a way to eliminate inhomogeneities and affect a substantial improvement. Such an investigation should be made with full scale charges and will require semi-plant equipment in order to be most effective.

The restrictive coating as finally developed is believed to be satisfactory. However, it has not been thoroughly tested under all conditions and in particular needs to be tested after severe cycling and thermal shock. Some improvement may be possible by using a less highly plasticized Paraplex AP-11 as the primary coat, by using a better grade of rubber tube, and by using cork discs which fit better. Close attention to small details and careful inspection at various stages of the coating process should do much to make a more reliable coating.

Two granulations other than the end burning solid have been considered and both should probably be investigated in more detail. It has been found possible to mold a cylindrically perforated grain which when restricted on the ends is neutral

burning. On static testing there was indication of restriction failure and so one of the major problems to be solved if such a grain is desired will be that of restriction. It is highly doubtful that this propellant could be used in this granulation in a rocket having high acceleration, but certainly could be used as a centrally-burning star center perforated grain of suitable design.

The difficulties likely to be encountered in connection with a star center perforated grain are in withdrawing the mandrel from the cured grain and in mounting the grain in the motor in such a way that it will be supported by the motor walls to prevent breakup from acceleration or pressure differentials. A suitable mandrel lubricant, such as perhaps soap-glycerin mixture, along with use of a tapered mandrel should be effective in solving the former. A scheme was suggested by Dr. L. P. Hammett for simultaneously mounting a star center grain in a motor and applying the restriction which appears remarkably simple. A somewhat simplified cross-sectional sketch is shown in Figure 16. The obturating pad would be of rubbery resin which must adhere well to the propellant and to the motor wall. The additional requirement is that the grain fit snugly against the motor wall at all temperatures. Possibly this could be accomplished by fitting the grain into the motor while the motor is at an elevated temperature and the grain is at -40°C., since the propellant does have rubbery characteristics and is capable of some deformation.

More suitable resins for use as binders might be found. Definite possibilities exist for improvement over 2851 Permafil in physical properties so as to decrease the somewhat crumbly nature of the grain. This is not disastrous in the case of the present compositions, but the problem of applying restrictive coatings would be somewhat simplified if an improvement could be made. The following resins are considerably better in this respect, but all contain volatile constituents.

	1	2	3
Aroclor 1254	-	35	34.3
Q166 resin	75	64	-
Styrene monomer	-	-	53.5
Ethyl cellulose 15 cps.	-	-	5.0
Ethyl phthalate	24	-	-
2851 Permafil	-	-	6.2
t-Butyl perbenzoate	1.0	1.0	1.0

All of these when filled with 75% $KClO_4$ burn vigorously. The liquid propellant can be cast into 3" diameter mandrel wrapped

cases of cellulose acetate and when cured the adhesion between propellant and case is very good. Several have been cycled between -40°C. and 60°C without separation. The cellulose acetate case serves also as the restriction, and, while the case is relatively expensive, the saving in manufacturing costs might be great enough to justify its use. Cases of polystyrene might well be considered since styrene is now cheap and abundant. If a plastic case is to be used as the mold and as the restriction it is desirable that some constituent of the liquid resin be capable of attacking and diffusing into the material of the case for a short distance, during the period before cure, to aid in securing a good bond to the propellant. The requirements for an ideal resin do not otherwise materially differ from the requirements outlined in Section II-B of this report.

The ideal rocket propellant would be smokeless, a goal which cannot be attained using $KClO_4$. The use of NH_4ClO_4 has been considered, but the HCl in exhaust gases from such a propellant causes formation of a mist. The only other possibility which suggests itself is the use of Ammonium Nitrate. Past experience at this laboratory gives rise to serious doubt as to whether a composition of the type needed for casting can be made to burn if Ammonium Nitrate is the oxidizing agent, particularly with resins now available. However, if a resin containing a relatively high percentage of $-NO_2$ groups, either as an explosive plasticizer or as part of the polymer molecule, were available the chances of success would be greatly improved. The resin must in addition be one which would be capable of withstanding the volume changes which occur as a result of reversible polymorphic transformations during temperature cycling.
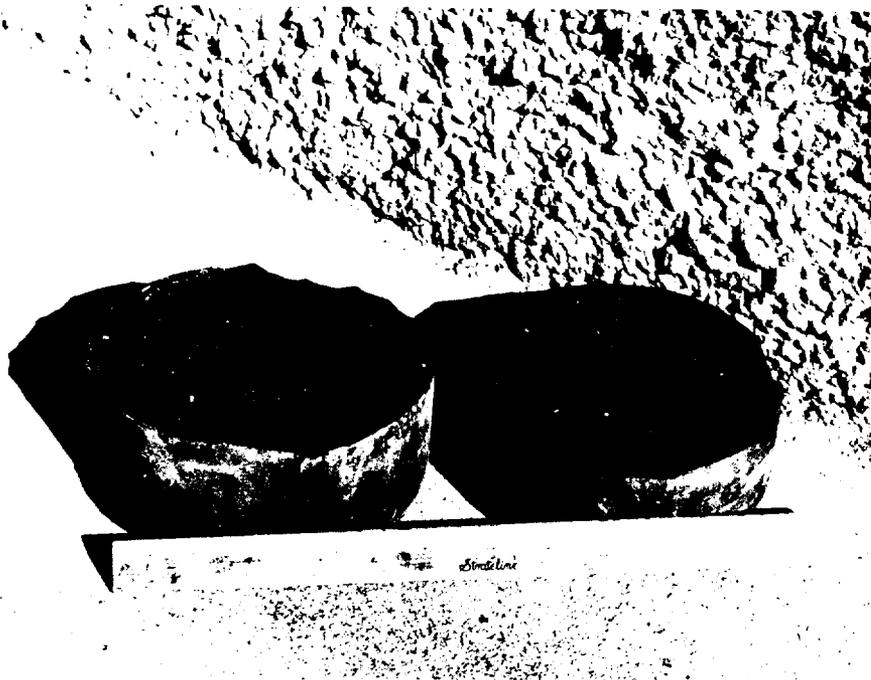
Plate 1. Partially Burned Grains Showing Roughening of Surfaces

Plate 2. View of Empty Mixer Showing Mixing Blades
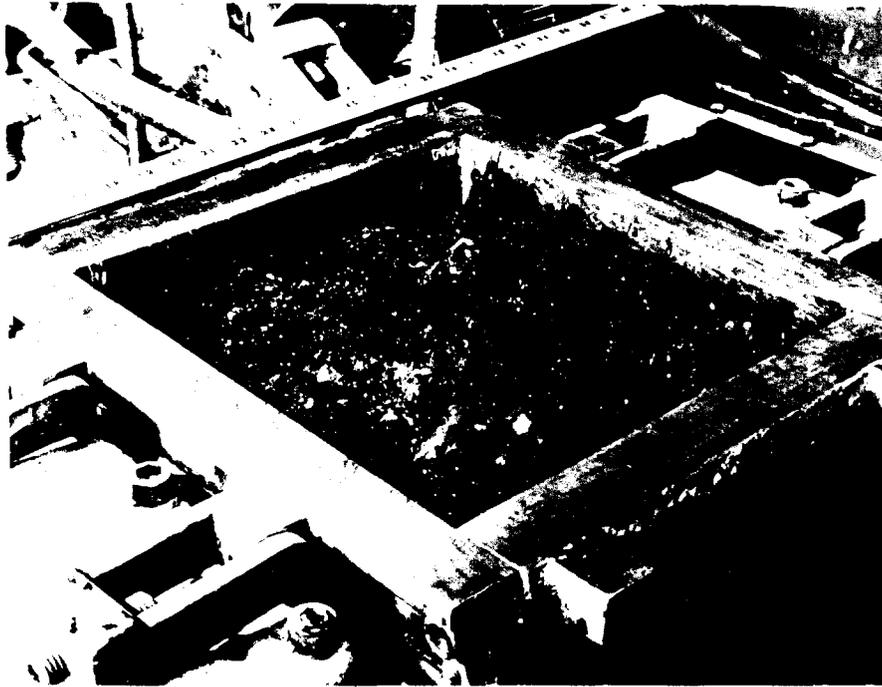
Plate 3. Appearance of Batch Immediately After Adding $KClO_4$
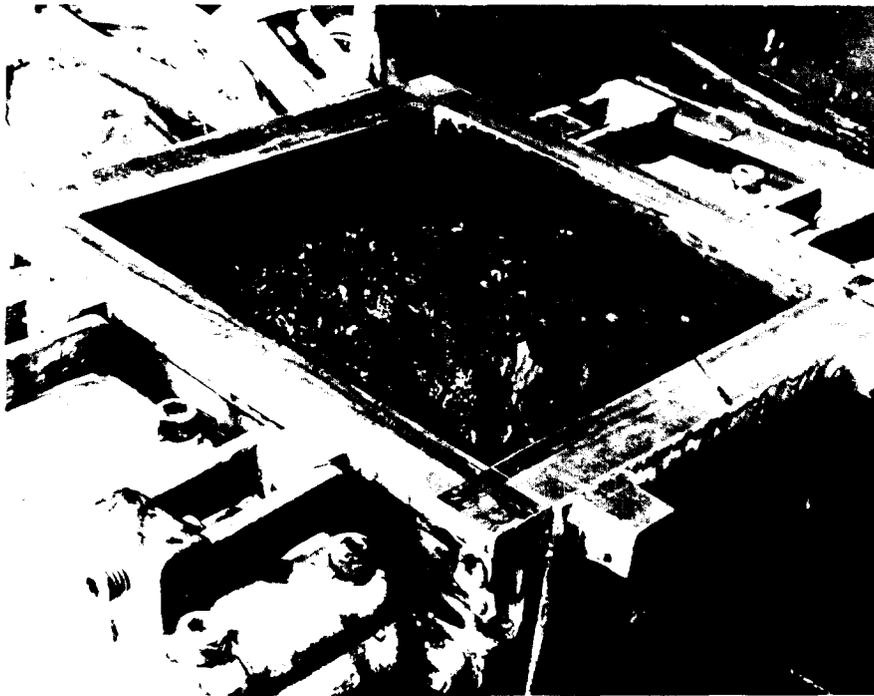
Plate 4. Appearance of Batch After One Half Hour Mixing
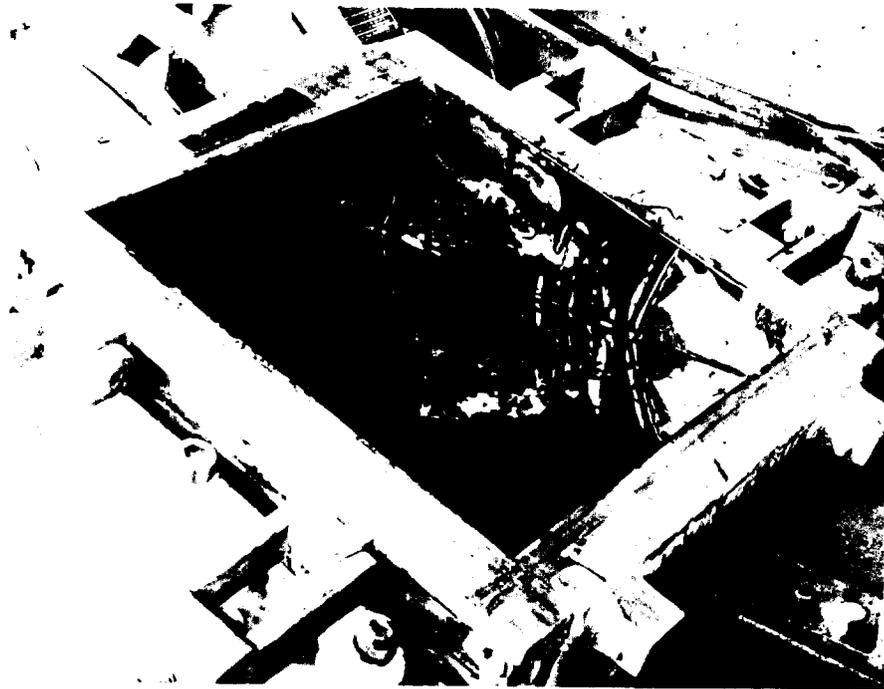
Plate 5.   Appearance of the Finished Batch

Plate 6.   Mixer Tilted for Casting
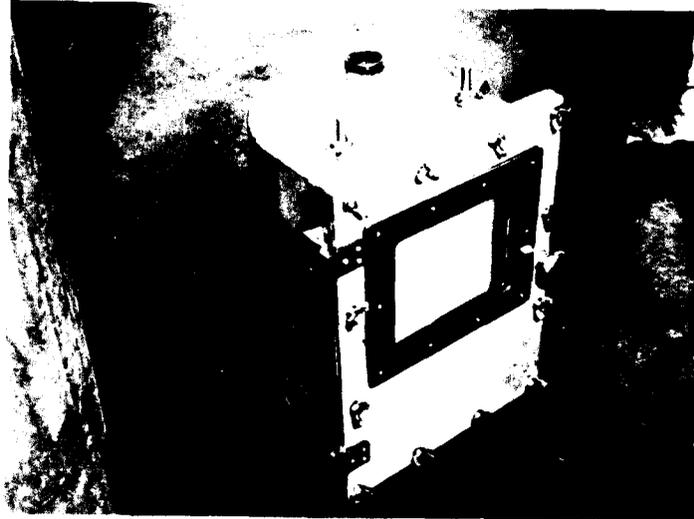
Plate 7. Vacuum Casting Chamber of Suitable Design
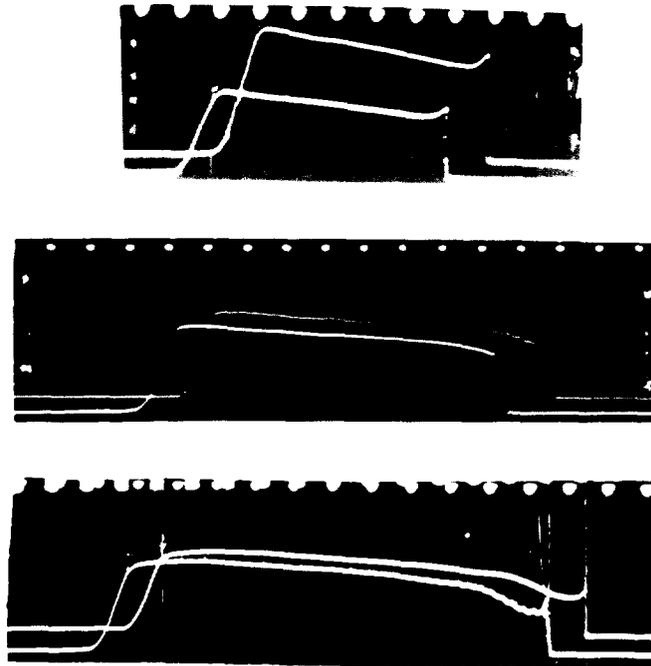
Plate 8. Typical Simultaneous Pressure-time and Thrust-time
Traces of 8.5" diameter End-burning Solid Grains
of Cast Perchlorate Propellant. (Time axis from
right to left)
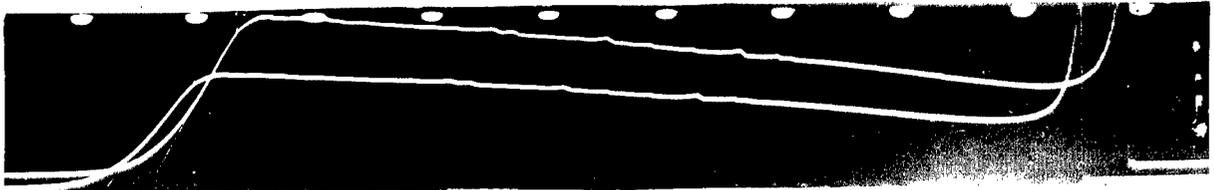
Configuration: Flat P_f/P_i =1.887 P_{max} =1626 PSI
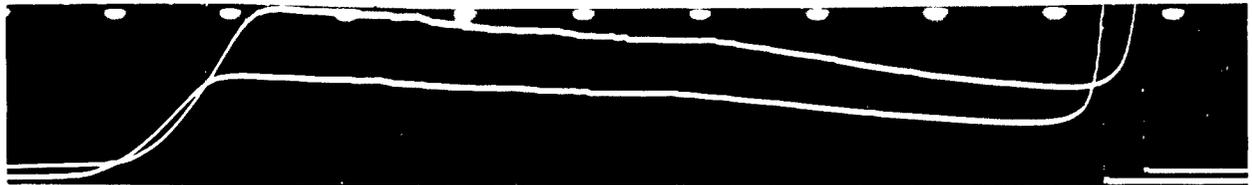
Configuration: Flat P_f/P_i =1.844 P_{max} =1565 PSI
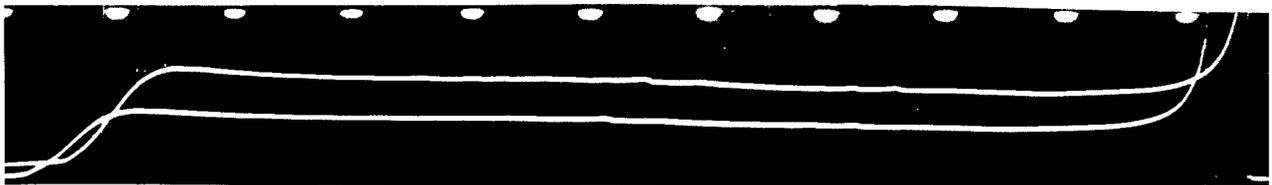
Configuration: 25°Cone P_f/P_i =1.140 P_{max} =980 PSI
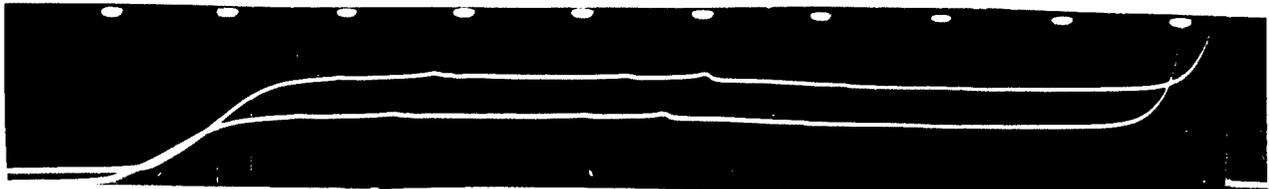
Configuration: 30°Cone P_f/P_i =1.009 P_{max} =995 PSI

Pressure-time Traces for Uncompensated
and Compensated 4" diameter Grains.
Time Axis from Right to Left.
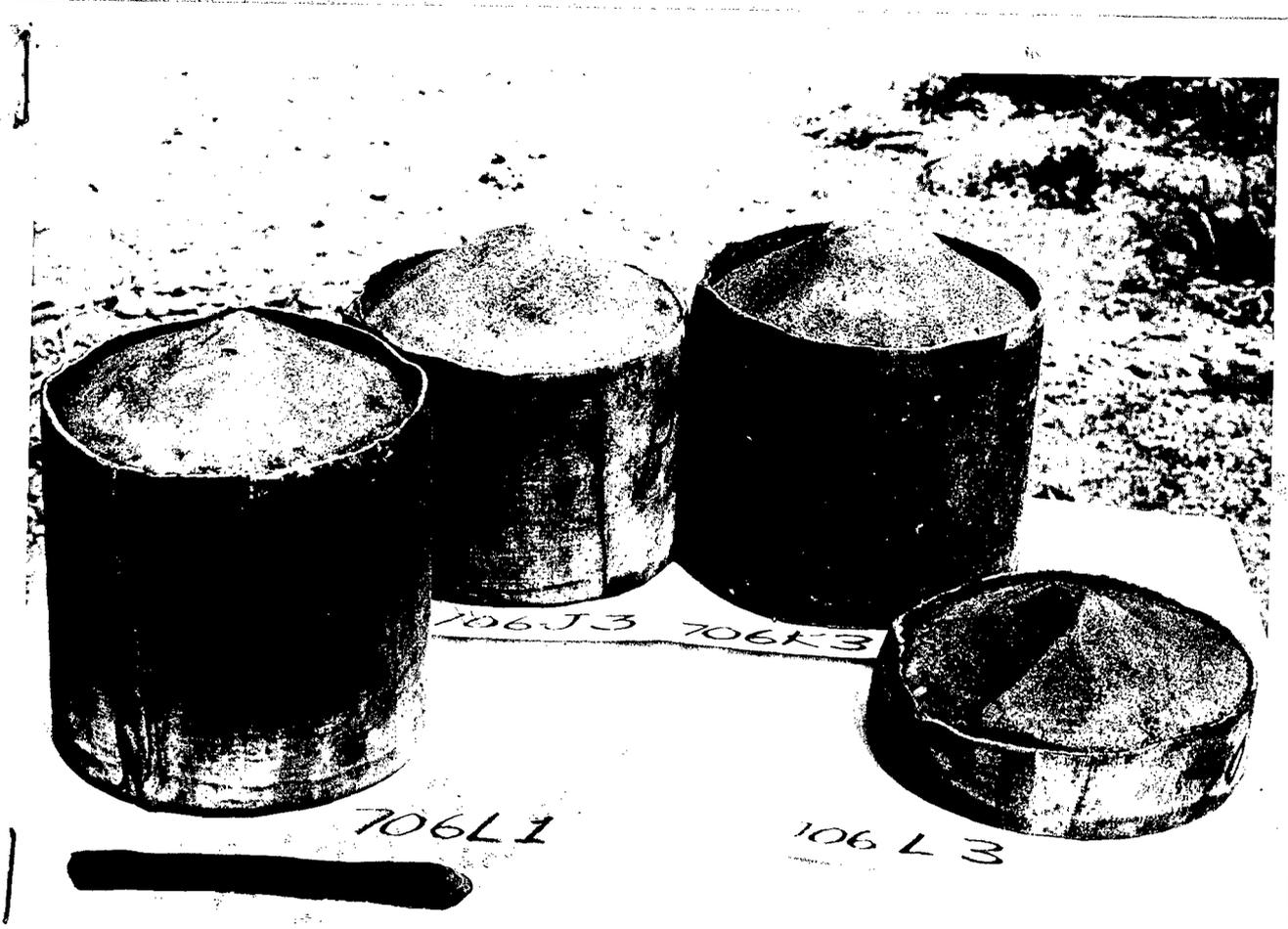
Plate 9

Plate 10

Partially Burned 4.5" Diameter Grains of an Early
Composition Showing Conical Surfaces Formed.

FIG. 1
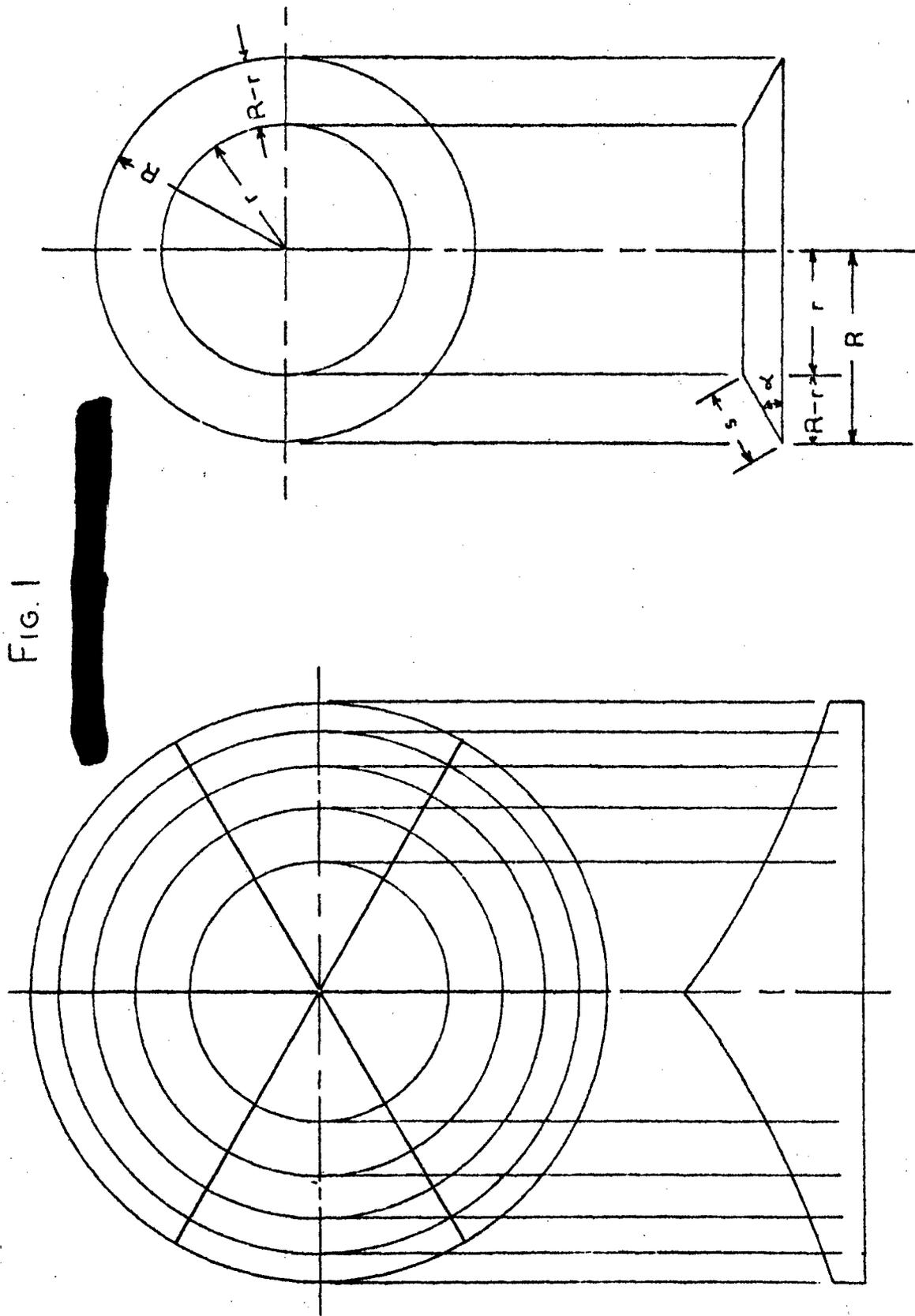
SINGLE ELEMENT

DIVISION INTO 30 ELEMENTS

AIR RESERVOIR

AIR LINE

MANOMETER

FUEL RESERVOIR

DISCHARGE TUBE

RECEPTACLE

Fig. 2 Viscosimeter

Fig. 3

74.5% KClO$_4$ S$_w$ =1200
0.5% C, Lecithin

78.5% KClO$_4$ S$_w$ =1200
0.5% C, Lecithin

74.5% KClO$_4$ S$_w$ =600
0.5% C

70% KClO S$_w$ =1200
5% Al, Lecithin

$\dfrac{3D\,\Delta P}{16L}$

$\dfrac{6V}{gD}$
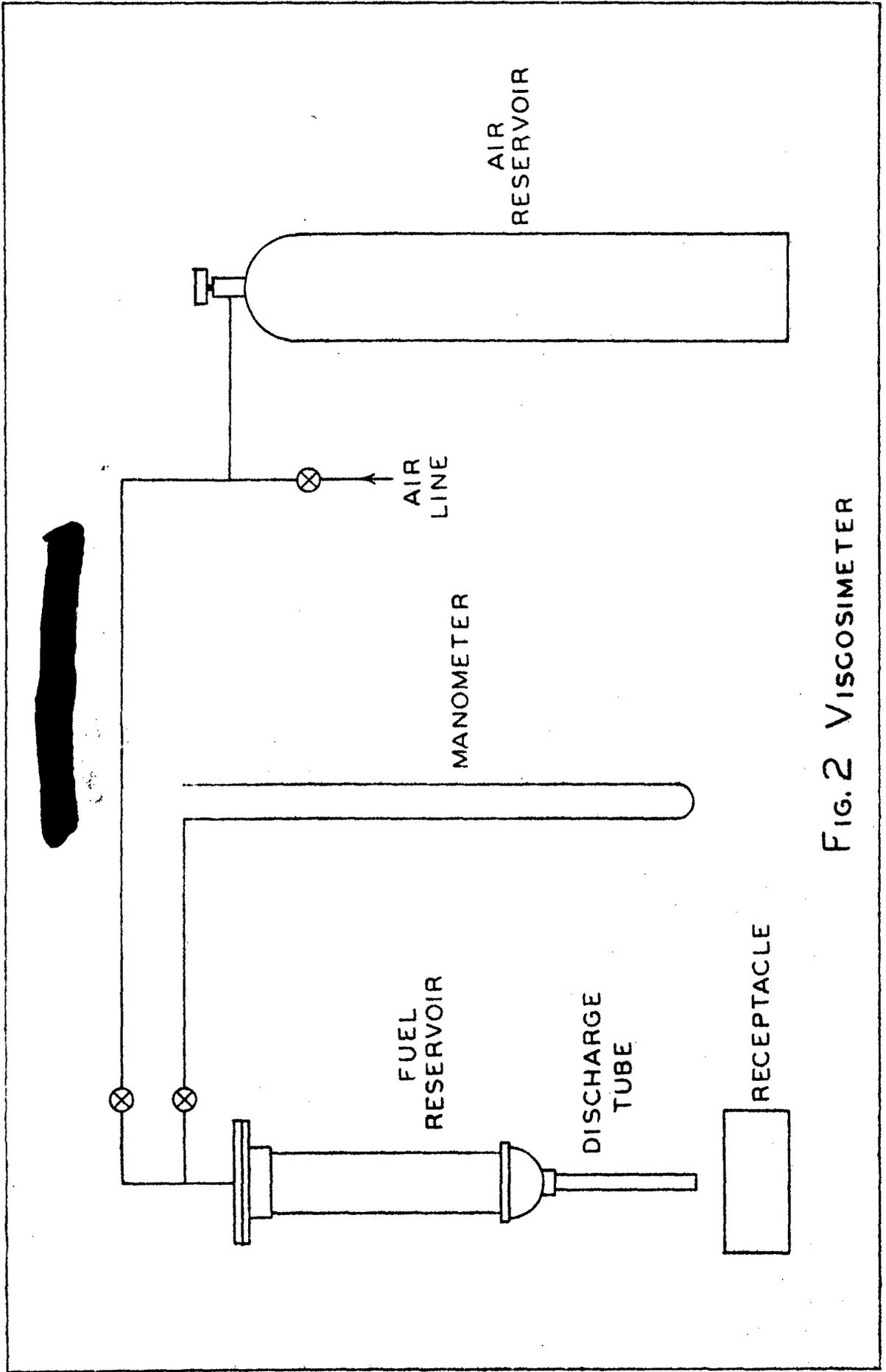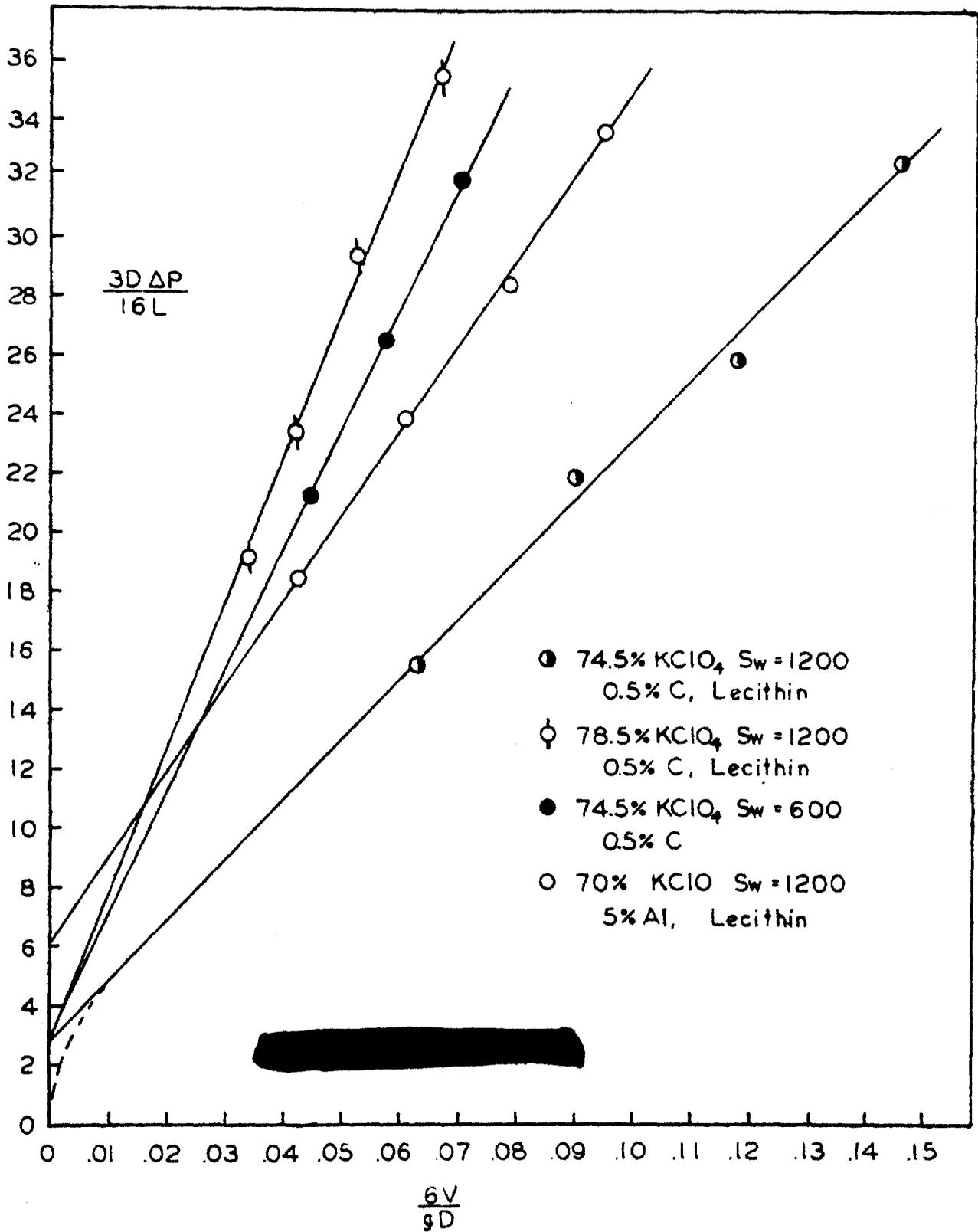
BURNING RATE OF ZV5273-5% Al COMPOSITIONS

FIG. 4A

R_{1000} (in./sec.)

Sw = 1760
Sw = 1100
Sw = 600

PER CENT $KClO_4$

FIG. 4B

R_{1000} (in./sec.)

75% $KClO_4$
70% $KClO_4$
65% $KClO_4$

SPECIFIC SURFACE
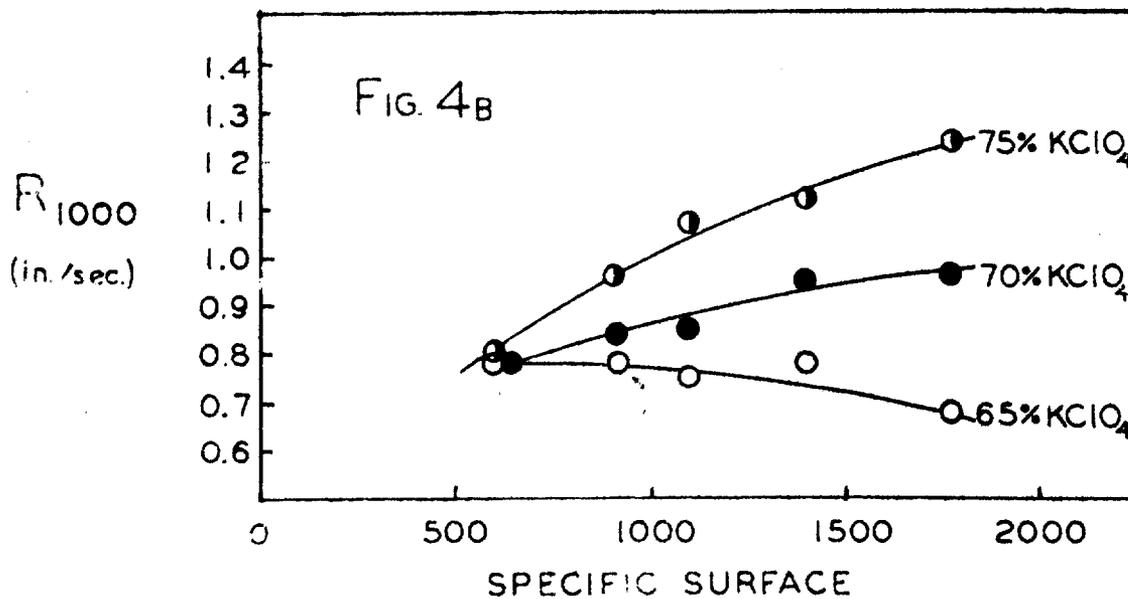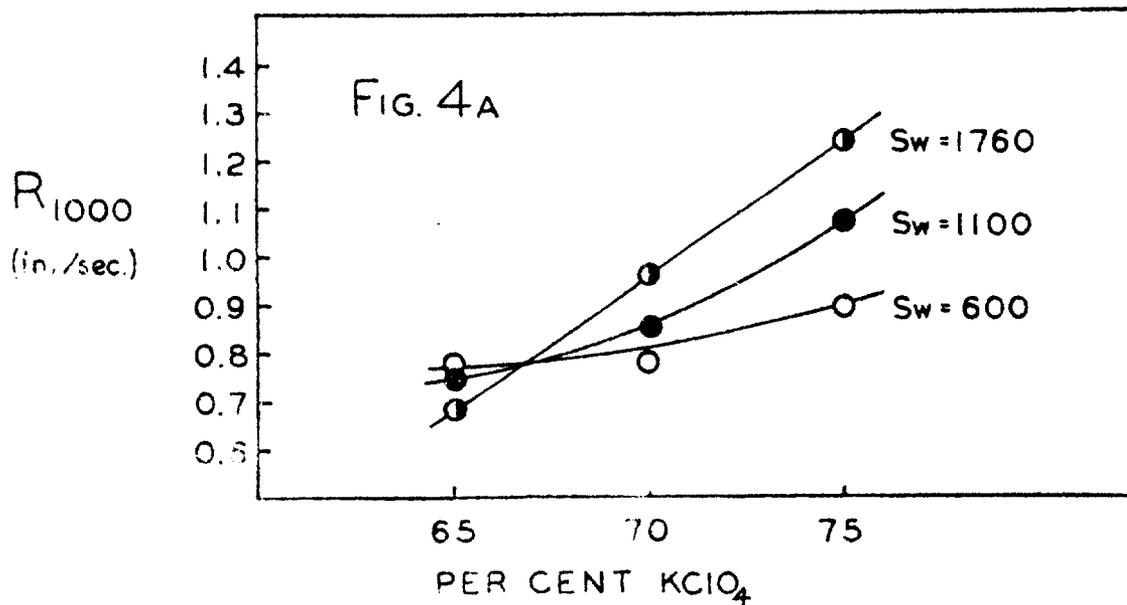
BURNING RATE OF 2851-0.5%C COMPOSITIONS

Fig. 5A

R_{1000} (in./sec.)

Sw = 570
Sw = 1150

PER CENT KClO$_4$

Fig. 5B

R_{1000} (in./sec.)

77% KClO$_4$
74.5% KClO$_4$
70% KClO$_4$

SPECIFIC SURFACE
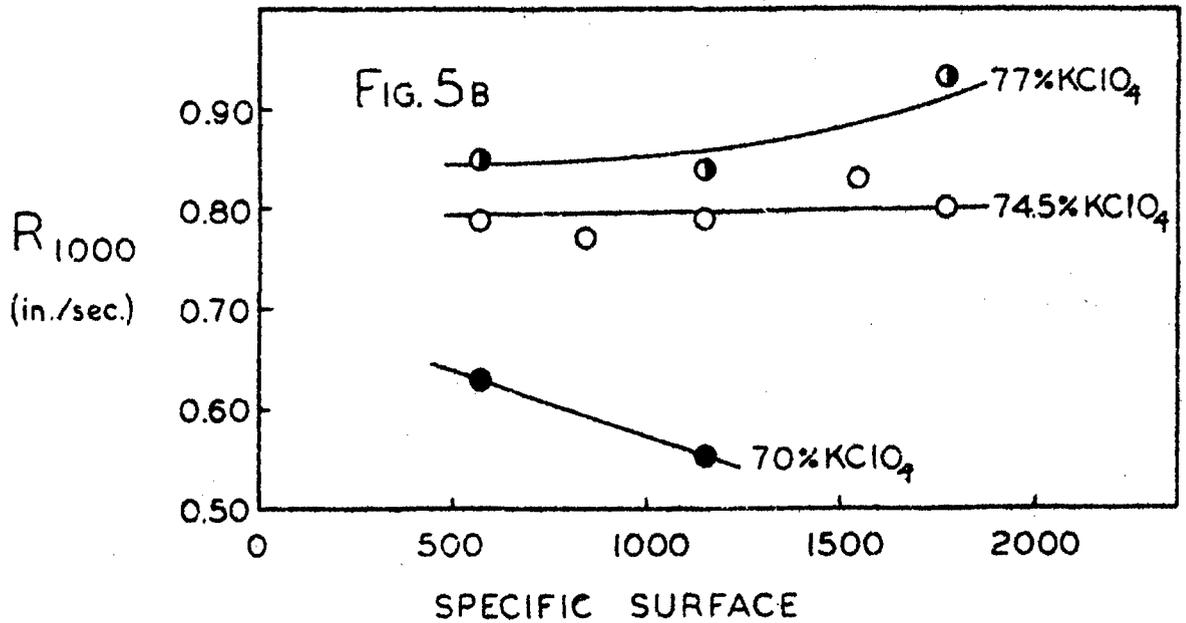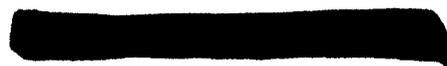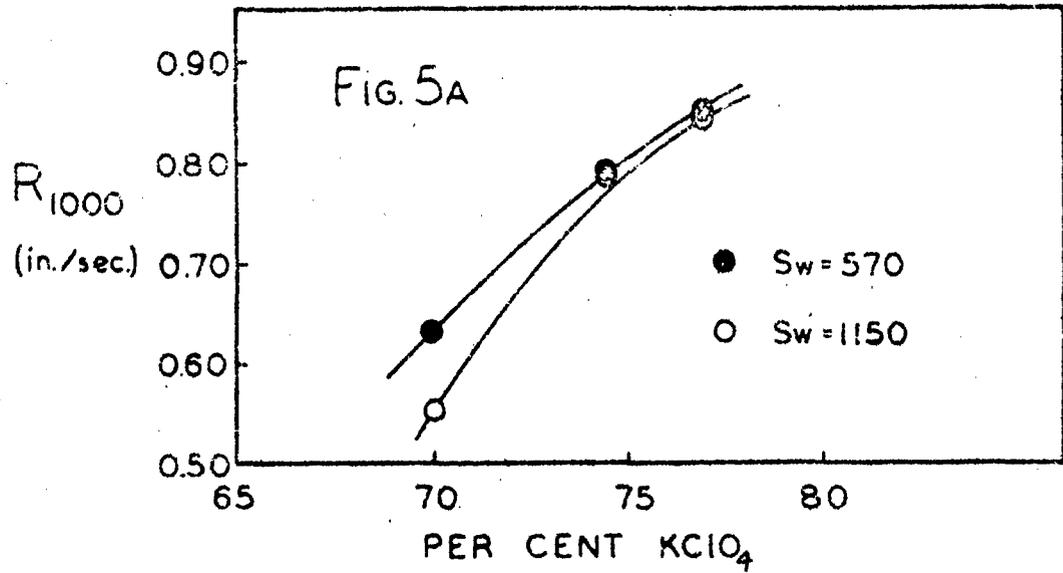
FIG.6 VARIATION OF SPECIFIC IMPULSE AT ZERO EXPANSION WITH PERCHLORATE CONCENTRATION

FIG. 7

VISCOSITY
(POISES)

PER CENT SOLIDS

FIG. 8

VISCOSITY
(POISES)

SPECIFIC SURFACE [CM.²/GM.]
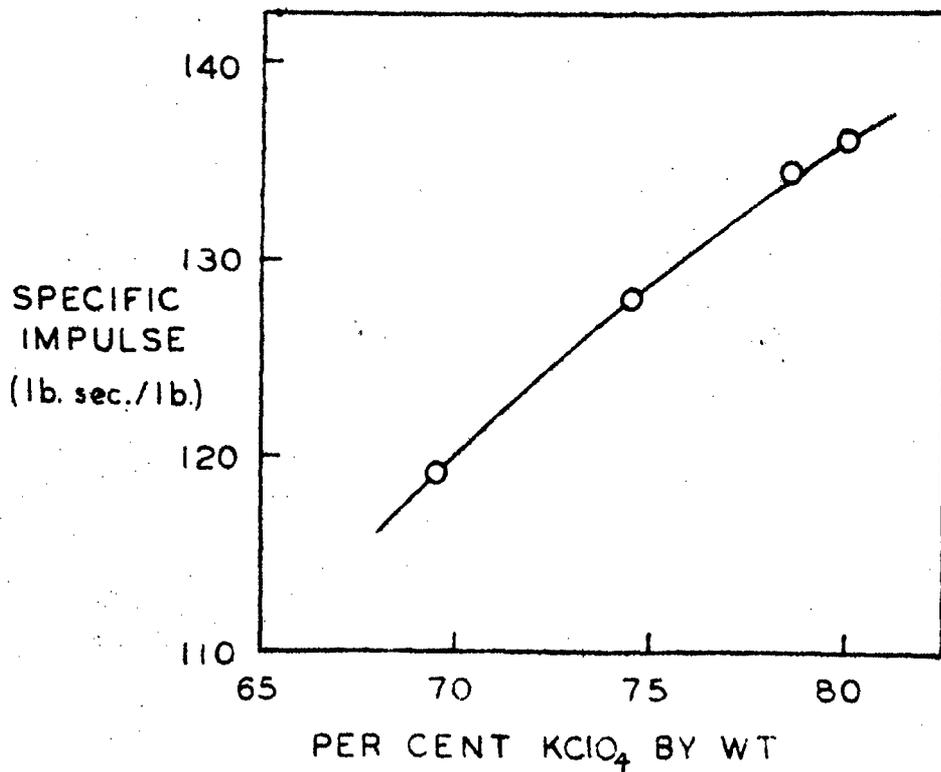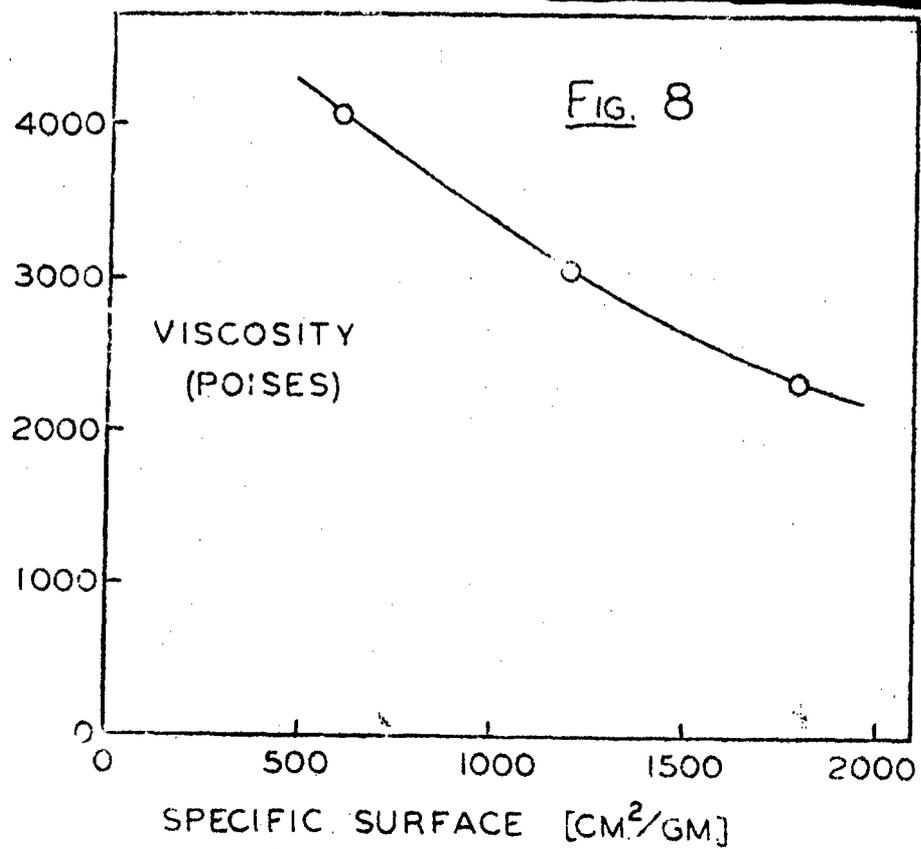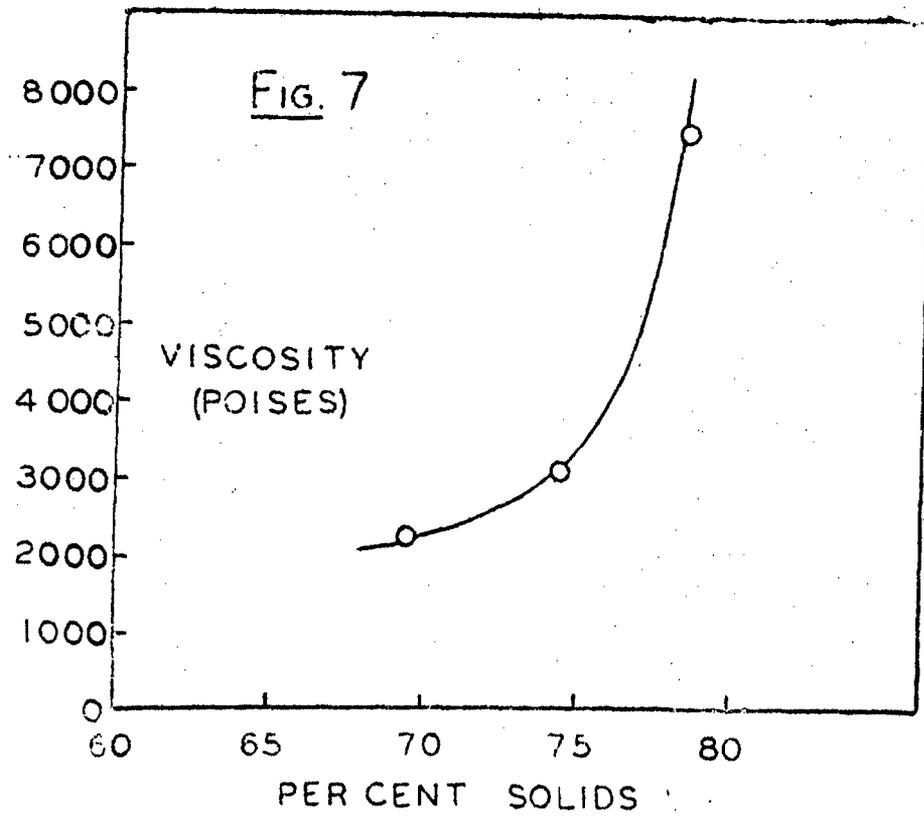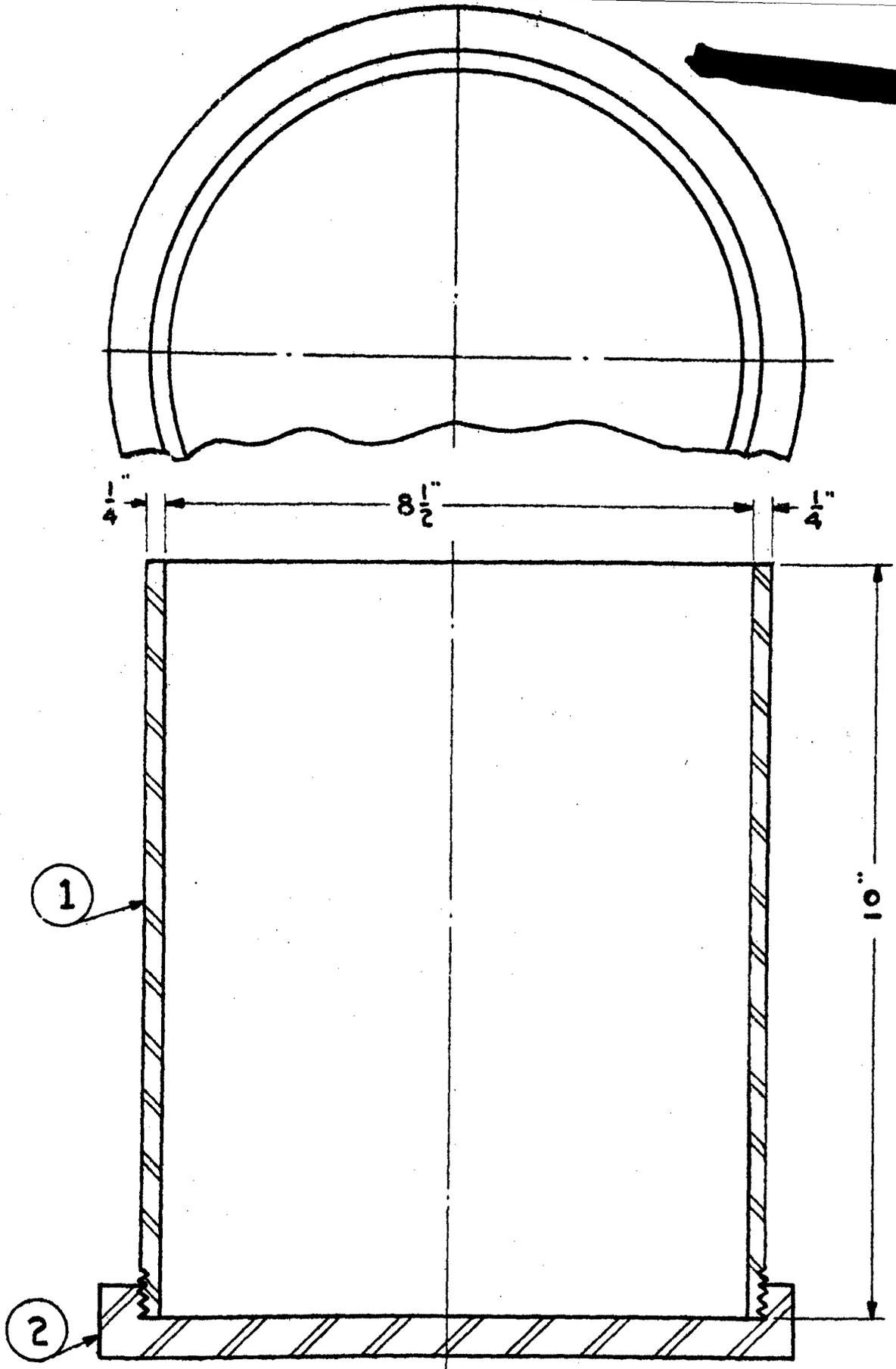
CAST PROPELLANT MOLD

FIGURE 9
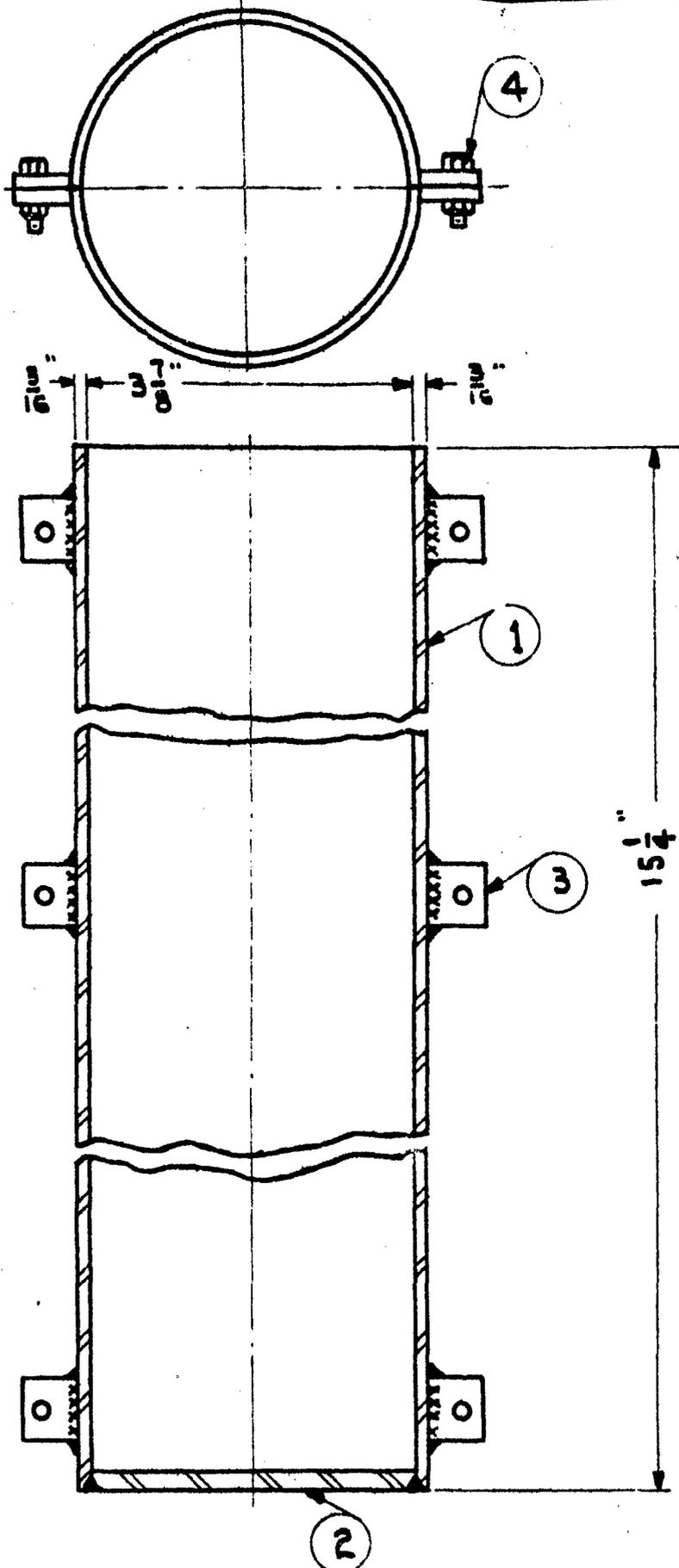
SPLIT MOLD FOR CAST PROPELLANT
FIGURE 10
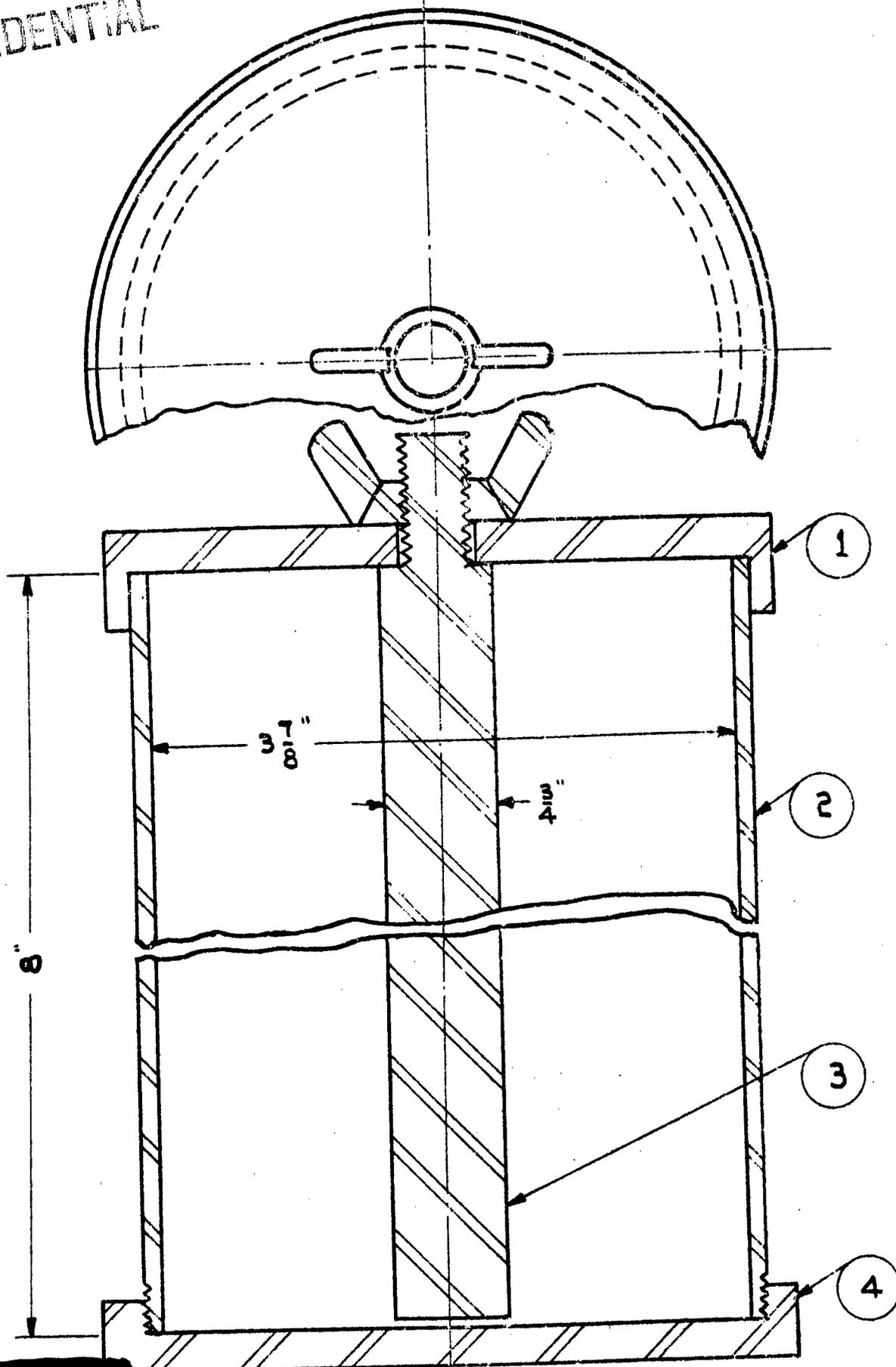
MOLD FOR PERFORATED GRAINS
FIGURE 11

FIG. 12 COMPENSATION OF PROGRESSION BY GRAIN DESIGN
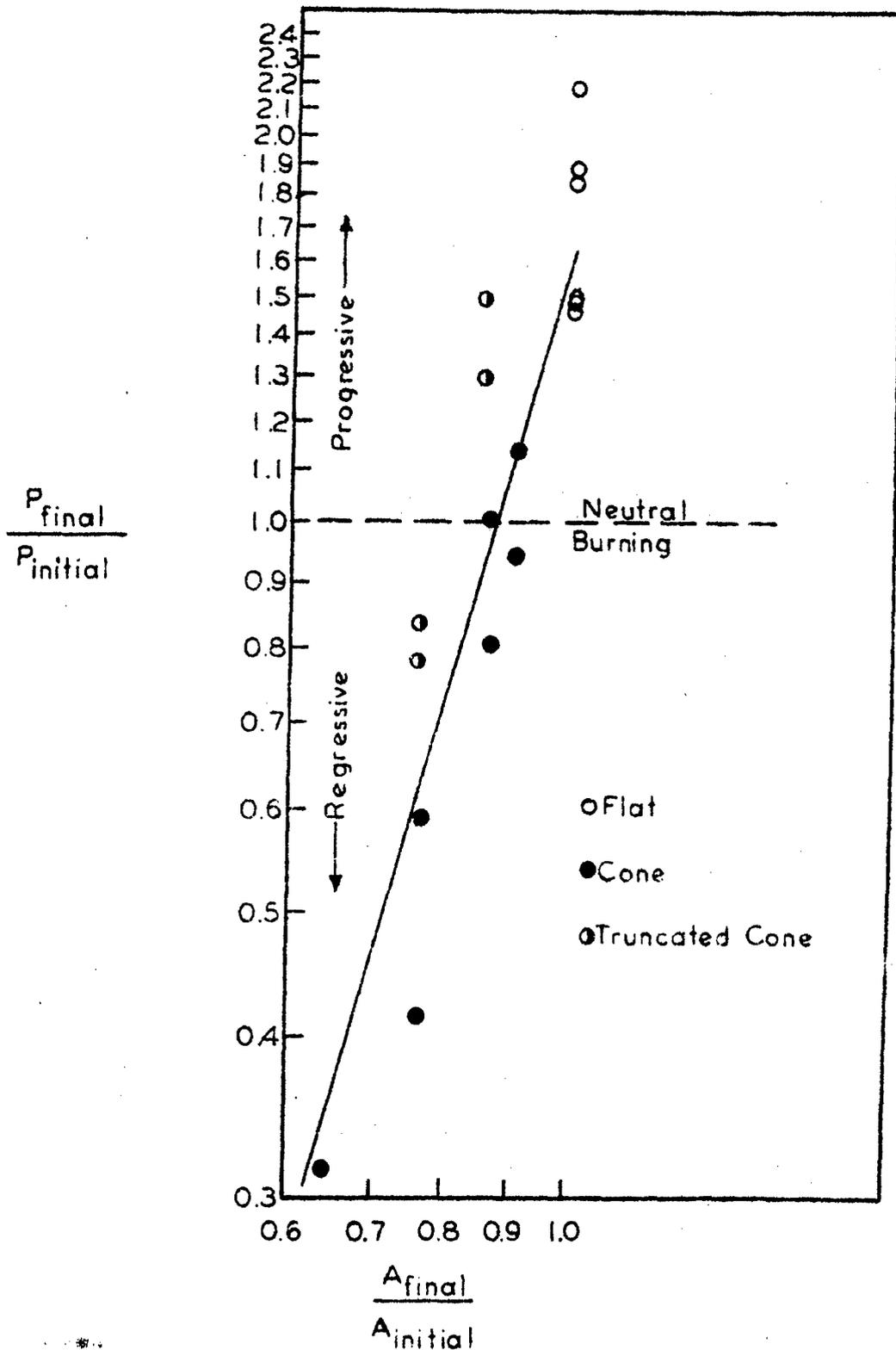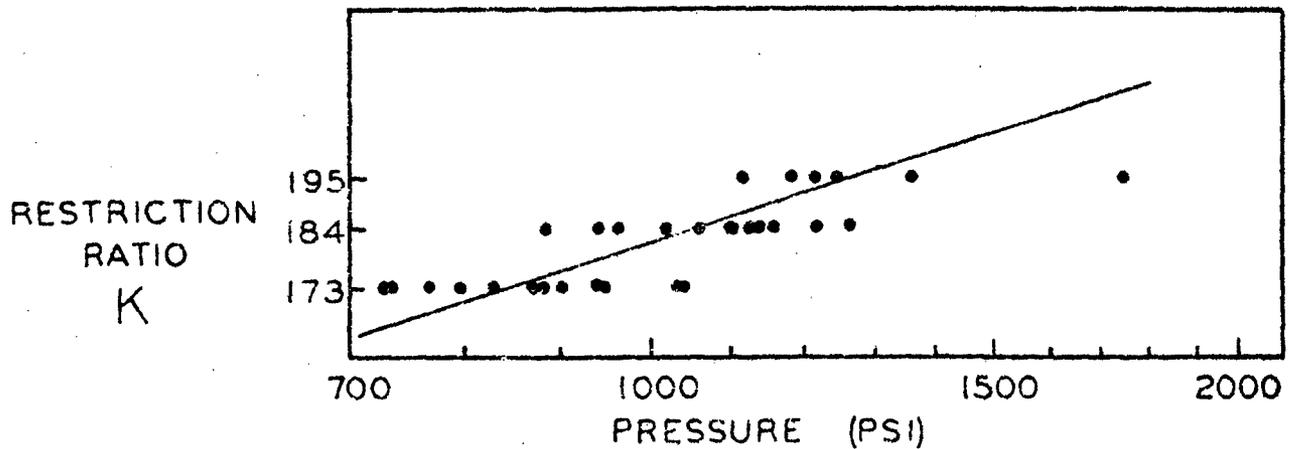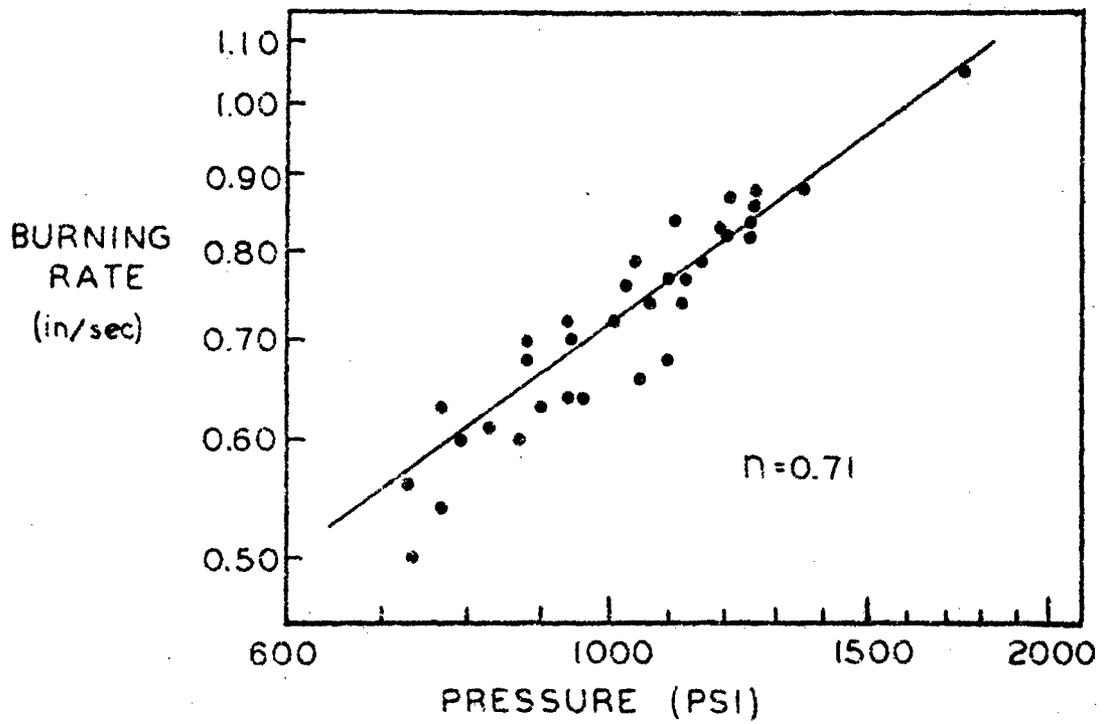
BALLISTIC PROPERTIES OF STANDARD COMPOSITION

FIG. 13
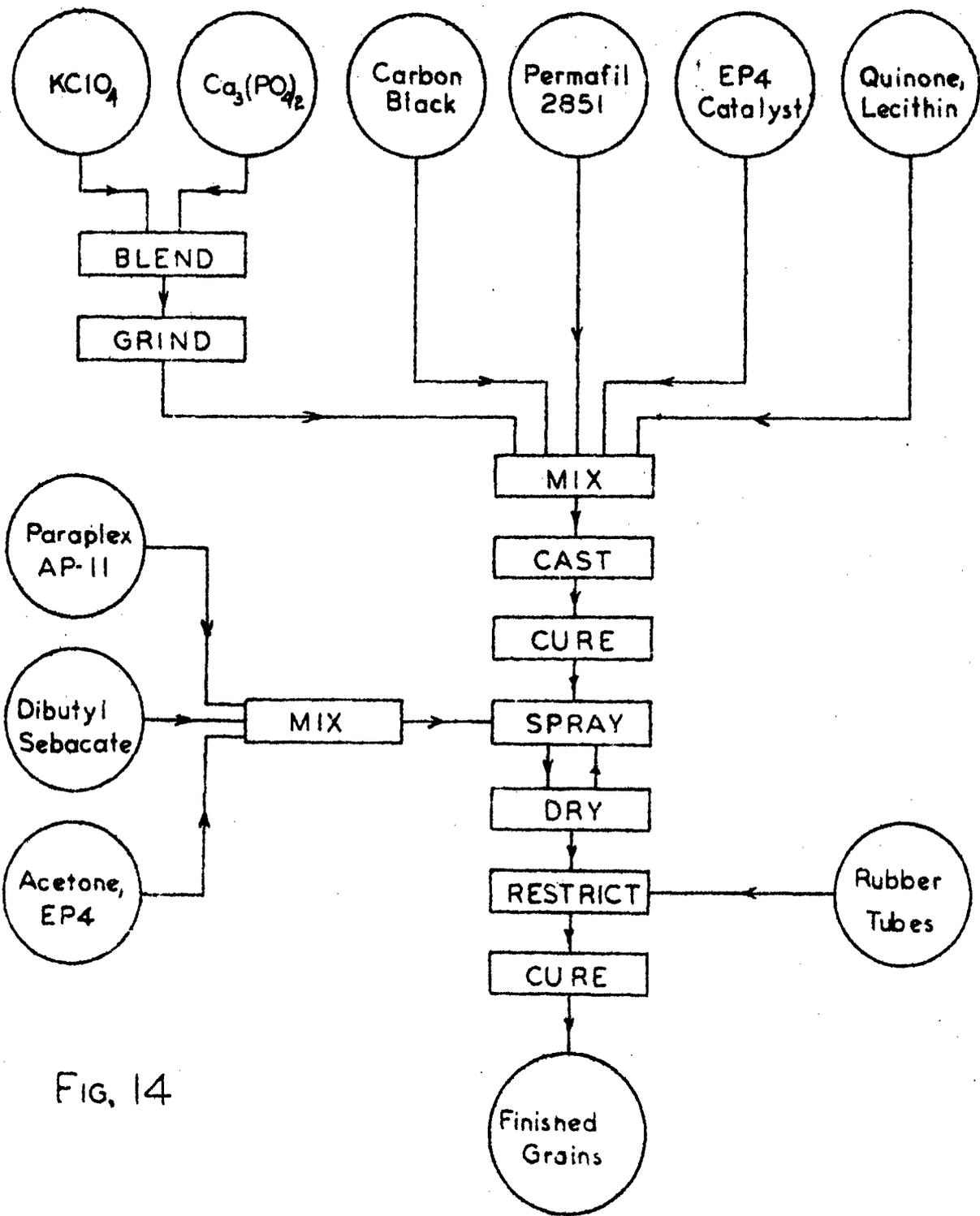
FIG. 14

PROCESS FLOW SHEET
FOR
CASTABLE PROPELLANT

FIG. 15

COMPLETED GRAIN

PROPELLANT
GRAIN

RUBBER
TUBE

PARAPLEX
COAT

CORK DISC

TAPE
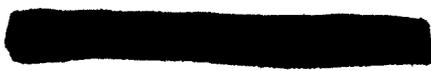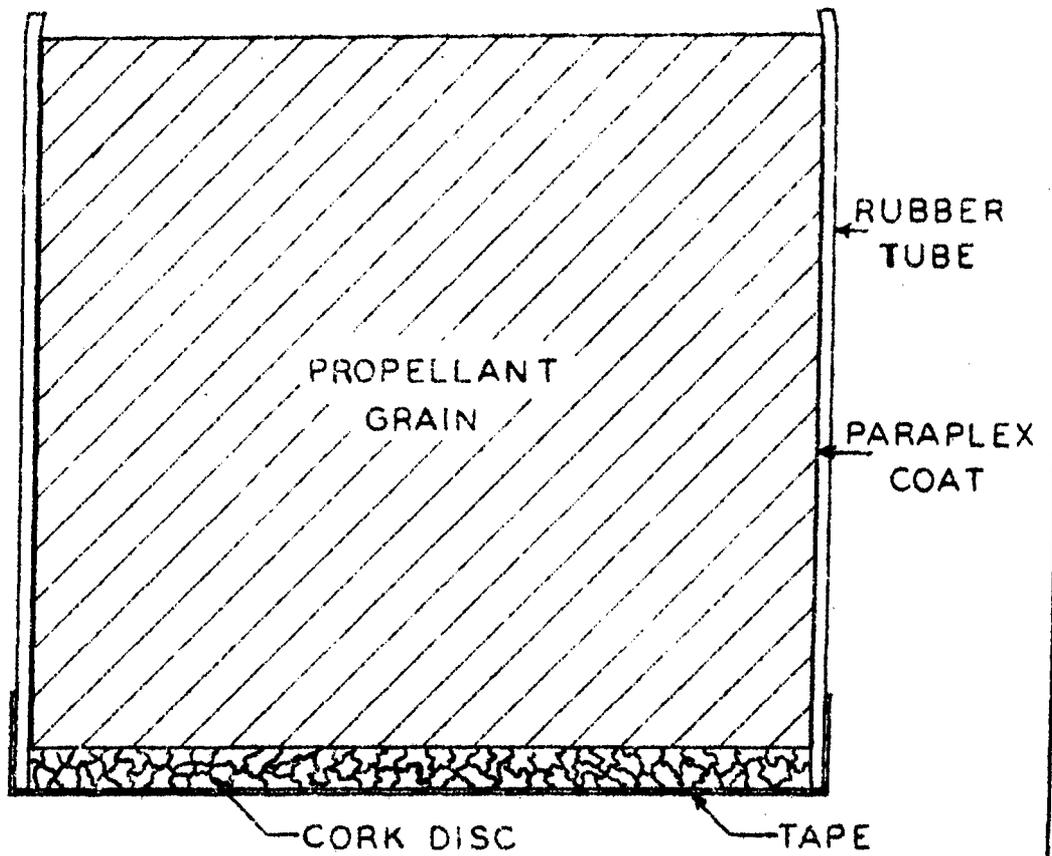
FIG. 16 METHOD FOR MOUNTING AND RESTRICTING CENTRALLY BURNING CHARGES

SOFT PLASTIC OBTURATING DISC

STEEL MOTOR WALL

CENTRALLY-BURNING GRAIN
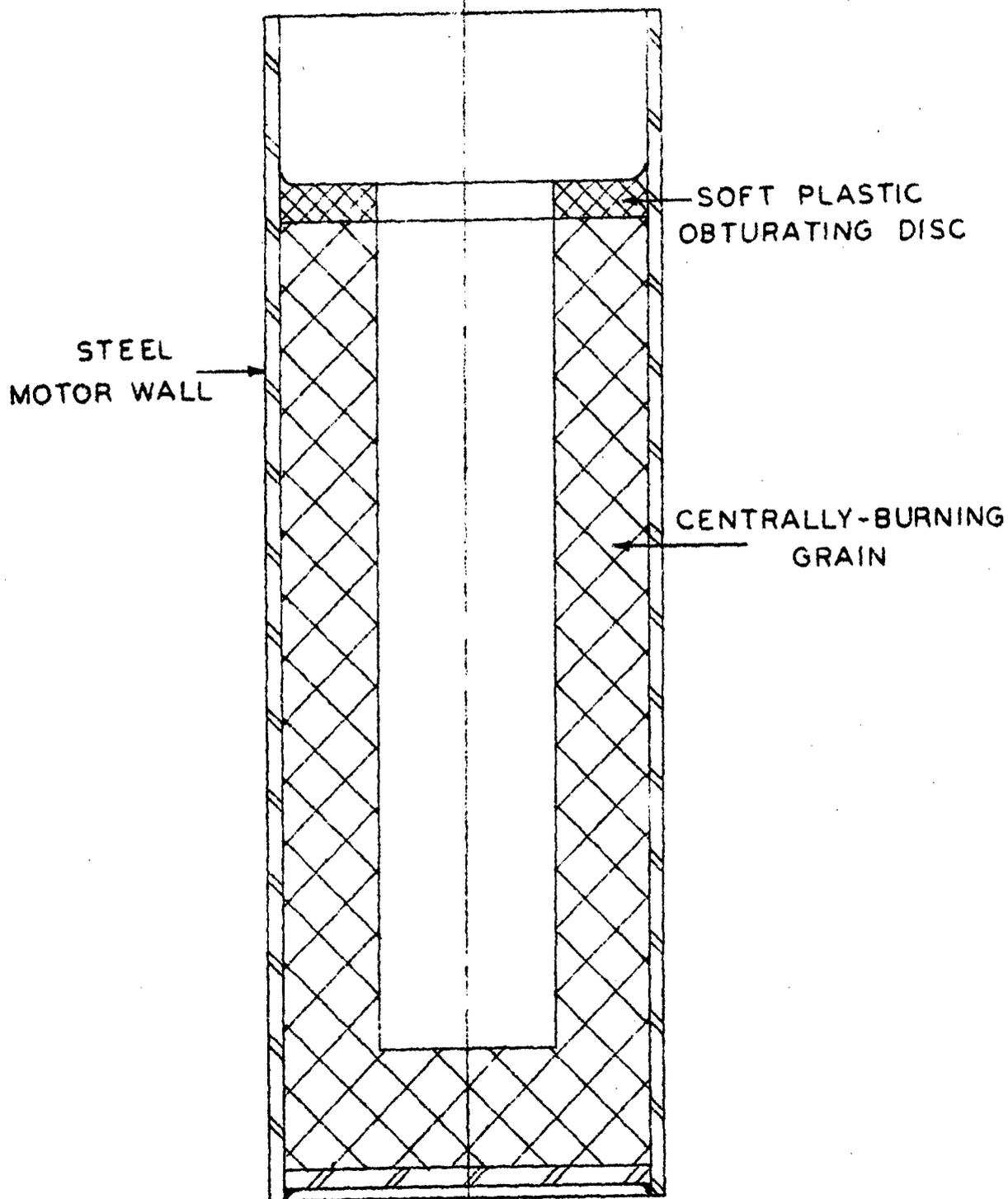
Appendix A

Cast Perchlorate Propellants with a Thermoplastic Resin Matrix.

A very definite possibility existed that some thermoplastic high polymer could be found which could be cast from a molten condition and which might nevertheless exhibit less change in its properties with temperature than do asphaltic materials. Inquiries were made of Dr. M. M. Brubaker and others of the duPont Experimental Station at Wilmington, Delaware, who suggested a mixture of ethyl cellulose with castor oil, which is referred to in the following as ECCO; another material was developed by the Experimental Station and coded as NDR-688. The compositions of these materials are

NDR-688   10% Butyl methacrylate polymer
            67.5% Castor Oil
            22.5% Hydrogenated castor oil

ECCO   25% Ethyl cellulose-Standard 7 cps.
            75% Castor Oil

These materials do not flow at 60°C. under their own weight and do not become brittle at -40°C. They have fair adhesion to steel. When mixed with 70-75% of pulverized potassium perchlorate a pourable mix is obtained, a temperature of 140°C. being required with ECCO and one of only 100°C. with NDR-688.

In initial tests small charges of these perchlorate-matrix mixes were made up in steel cups employing the technique used for preparing the Galcit propellant, including the use of a liner composed of the unfilled matrix material. The products behaved so erratically as to be completely unusable as a propellant, giving something approaching steady state burning only over a very narrow range of restriction ratios, progressing to very high pressures at higher restriction ratio values and dropping in pressure to the point of cessation of burning at lower values. Nevertheless, partially burned charges obtained either at high or at low pressures showed smooth flat surfaces with no evidence of burning down the wall or down the interface between liner and charge when the ECCO matrix was used. The NDR-688 compositions were less satisfactory in this respect, since burning frequently went down the propellant liner interface.

i

The reason for this erratic behavior appeared when Crawford closed bomb burning rate measurements were made. It was found that the exponent in the burning law for this composition had a value of 0.80. With so high an exponent the system becomes so sensitive to the burning surface and so slow to readjust itself to a new steady state when small variations in burning surface occur that for all practical purposes the system is an unstable one.

By making use of the closed bomb burning technique, experiments to determine the effect of various additions upon the exponent and burning rate could be carried out rapidly. Data from a series of experiments are summarized in Table I. All these compositions were made with $KClO_4$ having a specific surface of about 600 square centimeters per gram. All compositions containing large percentages of KNO_3 failed to burn in the bomb. When 10% and 17% of KNO_3 were substituted for $KClO_4$, a straight line could not be drawn through the points of a logarithmic plot of burning rate against pressure, some sort of break occurring between 1000 and 1500 psi.

These results show that a very material reduction in exponent may be obtained by the addition of powdered reducing agents, and that a particularly favorable effect is produced by a small proportion of aluminum flake. The composition

     25% ECCO
      5% Aluminum (alcoa albron powder std., unpolished 606-A)
     70% $KClO_4$

was therefore investigated in more detail.

Table II contains data from the closed burning rate bomb showing the influence of $KClO_4$ concentration and particle size on rates of burning of ECCO compositions.

The ECCO binder is prepared by adding the ethyl cellulose over a period of one to two hours to the castor oil held at a temperature of 160-170°C. in a vessel equipped with a slow speed propellor type stirrer. Stirring is continued until a clear solution is obtained, usually 4 to 6 hours. 0.5% of lecithin is added as a surface active agent.

The motors employed in the following experiments were 4" in inside diameter and the charge cast into them was 3.75" deep. The motors were lined, using the Galcit technique, by pouring a mixture of ECCO and 2% aluminum flake at a

temperature of 160°C. into the cold motor and rotating the motor while pouring out the excess liner in such a way as to obtain a uniform layer 1/16" to 1/8" thick adhering to the walls. The motors were allowed to cool for an hour or more before adding a propellant charge. The aluminum was used to make the liner opaque; there is no proof that this is necessary.

The propellant was prepared in a sigma type mixer heated to 100°C. by means of steam. The EC60 is allowed to soften for several minutes, the aluminum is then mixed in, and the potassium perchlorate is finally added gradually over a period of 15-20 minutes. The mixing is continued for an hour under a vacuum of 27 to 29" of mercury. The product is then transferred to an open kettle and heated to a temperature of from 140-150°C. It is then poured into the lined motor down a slightly inclined trough so arranged as to minimize folding over of material with entrapment of air. The loaded motors are allowed to cool from 20 to 24 hours in an environment of about 25°C. and the burning surface is then shaved smooth and flat. It must be emphasized that the aluminum and potassium perchlorate must not be mixed dry, since the dry mixture is relatively sensitive to explosion by impact.

The propellant is a plastic material with a dull metallic appearance. The theoretical density is 1.819 gm/cc. Densities measured by immersion have been 98-99% of the theoretical.

At 60°C. the propellant is somewhat soft and rather easily deformed, while at -40°C. it becomes rather hard but non-brittle. The liner is somewhat softer and more tacky. A number of tests of the flow at 60°C. when placed on the side were made using charges 4" in diameter and 3.75" long cast directly into lined motors. These included some variations in the viscosity and amount of ethyl cellulose used and are summarized in the following table.

Composition of Matrix	Test Result

75-25 Castor Oil-Ethocel 7cps. Liner parted from motor wall at top at 12 days. Top receded 3/32". Bottom flowed out 3/32".

79-21 Castor Oil-Ethocel 10cps. Liner parted from motor wall at top at 27 days. Top receded 1/8". Bottom flowed out 5/32".

75-25 Castor Oil-Ethocel 10cps. Liner and fuel parted at top on 29th day. Top, no recession. Bottom flowed out 7/32".

An 8.5" x 8" grain was made by casting into a 9 inch I.D. fiber carton with about a 3/16" liner. The matrix was 75-25 Castor oil-Ethocel 10 cps. After 4 days at 60°C. on the side the liner parted from the carton, adhering to the grain, while the top receced and the bottom flowed out. Several grains were fired after separation of the liner from the motor wall and did not develop excess pressures.

Sensitivity and stability data for this composition are summarized in the following table.

Ignition Temperature	>360°C.
135°C. Thermal Stability	OK 24 hours
160°C. Thermal Stability	OK 85 hours
120°C. Vacuum Stability	0.33 cc gas/5 gm. in 48 hours
Impact Sensitivity Bruceton design No. 12	157-171 cm.

Values reported for impact sensitivity are drop heights for 50% explosion. With design 12 values of 39 cm. were obtained for Tetryl and 145 cm. for TNT.

Charges 1-5/8" x 5" cast into cardboard tubes were neither detonated nor ignited by a 90 gm. Tetryl booster pellet exploded in contact with one end of the charge while the other rested on a steel plate. Similar charges confined in 2" O.D. x 1-5/8" I.D. steel tubes were likewise neither detonated nor deflagrated by a 90 gm. Tetryl booster.

Test firing data for this composition are summarized in
Table III. Preliminary data on specific impulse and related
properties follow.

Restriction Ratio	200	170
Average Pressure	2130	1105
Expansion Ratio	6	6
Specific Impulse	187	177
Thrust Coefficient	1.51	1.48
Discharge Coefficient	0.0081	0.0083

Considerable difficulty was experienced in early test firing
with erosion of nozzles of steel and copper of good contour.
Steel nozzles with molybdenum insert throats were found to
stand repeated firings of 4 second duration at pressures up
to 3000 psi.

As noted in Table III several shots have been fired at
-45°C. with satisfactory results. These, with the few
shots at 60°C., suffice only to establish that the tempera-
ture coefficient of burning rate at constant pressure is
very small. The reproducibility of the material is perhaps
as good as is to be expected in the light of the decidedly
imperfect casting technique.

While this propellant represented an improvement over
existing cast perchlorate propellants in its usefulness at
extreme high or low temperatures, it obviously retained
the undesirable property of eventually flowing at 60°C.
Moreover, there was no way of predicting the magnitude of
the effect in larger charges. Consequently it was decided
to concentrate our entire effort on the development of a
propellant based on a thermosetting polymer in order to
eliminate this uncertainty.

Table I - Appendix A

Influence of Additives on Exponent and Burning Rate in ECCO Compositions

Composition	n	R_{2000}
30% ECCO 70% $KClO_4$	0.79	1.42
28% ECCO 2% Carbon* 70% $KClO_4$	0.79	1.46
25% ECCO 5% Carbon* 70% $KClO_4$	0.75	1.12
18% ECCO 12% Carbon** 70% $KClO_4$	0.72	1.20
15% ECCO 15% Carbon** 70% $KClO_4$	0.68	0.98
20% ECCO 20% Carbon** 60% $KClO_4$	0.69	0.83
25% ECCO 5% Al flake 70% $KClO_4$	0.65	1.40
25% ECCO 10% Al flake 65% $KClO_4$	0.61	1.30
25% ECCO 5% NH_4 Picrate 70% $KClO_4$	0.68	1.46
20% ECCO 15% NH_4 Picrate 65% $KClO_4$	0.71	1.37

*Excello
**Thermax

Table I - Appendix A (Continued)

Composition	n	R2000
25% ECCO 5% Al flake 5% Carbon 65% KClO$_4$	0.64	1.22
25% ECCO 5% Nitroguanidine 70% KClO$_4$	0.76	1.37
25% {50% Castor Oil, 25% DNT Oil, 25% Ethocel} 5% Al flake 70% KClO$_4$	0.58	1.45

Table II - Appendix A

Change of Burning Rate with Specific Surface for Some ECCO Compositions

Composition	R_{2000}			
	S_W=650	S_W=910	S_W=1100	S_W=1400
30% ECCO (10 cps.) 5% Al flake 65% $KClO_4$	1.05	1.08	1.00	1.12
25% ECCO (10 cps.) 5% Al flake 70% $KClO_4$	1.36	1.34	1.47	1.46
20% ECCO (10 cps.) 5% Al flake 75% $KClO_4$	1.20	1.26	1.46	1.66

Table III - Appendix A

Test Firing Data for 4" x 3.75" Solid Castings of ECCO Propellant

K_{Before}	K_{After}	Temp.	Pav.	R	Progression % Per Inch Web	Remarks
162	172	25°	1630	1.19	5.1	
175	180	25°	1575	1.11	0.0	
163	170	25°	1025	0.82	3.2	
190	200	25°	1950	1.35	7.4	
164	181	25°	1790	1.16	13.3	
166	170	25°	1505	1.04	3.4	
170	170	25°	1105	0.82	6.7	
200	205	25°	2130	1.28	12.0	
215	216	25°	2680	1.57	?	Moly. in steel ok. (Shot 1)
211	215	25°	2295	1.42	?	Graphite in steel ok.(Shot 1)
182	181	25°	1565	1.20	2.3	---
216	216	25°	2220	-	10.0	Moly. in steel ok. (Shot 2)
217	218	25°	2190	1.55	2.9	Moly. in steel ok. (Shot 3)
213	210	25°	2400	1.59	10.0	Graphite in steel. Grooving on Shot 2.
163	163	60°	1170	0.97	3.7	Stored 18 hrs. at 60°C. on side.
161	161	60°	1520	1.10	0.0	Stored 18 hrs. at 60°C. on side.
163	166	58°	1650	1.11	2.9	Stored 96 hrs. at 60°C. on side.
205	201	-40°C.	1675	1.15	11.2	
190	194	-45°	1330	0.94	0.0	
190	193	-45°	1340	0.99	7.4	
190	194	-45°	1395	0.97	33.1	
194	194	-43°	1400	1.03	0.0	
194	199	-43°	1140	0.79	0.0	
193	198	-43°	1380	1.01	?	

Appendix B

Experiments on Alternate Types of Restriction

The possibility of still further simplifying the process of propellant manufacture by casting a liquid propellant directly into a suitably prepared motor and bonding it to the motor wall during the cure reaction has been attractive. Here the motor wall would serve as the restriction, and the grain would be an end burning solid cylinder or a centrally burning perforated cylinder.

The resin desired for this use would have essentially the properties enumerated in Section II-B above. It would, however, be very flexible at all temperatures within the range for use, would shrink as little as possible during cure, and would adhere very strongly to steel or to another material which might be interposed between the propellant and the steel.

Most of the resins of Section II-B were tested for adhesion to steel when filled with 70% of $KClO_4$ using cylindrical steel cups 2-3/4" diameter. Many adhered well, notably those based on styrene, and Q166, BRS 16631, and Paraplex P-10. Others such as Cardolite resin, NDRC-Westinghouse Potting Compound, and the Permafil resins adhered only moderately well. All of them, however, shrank sufficiently on cure that they pulled loose from the motor wall or developed internal cracks. Moreover, none of them was sufficiently rubbery over the entire range of temperatures to absorb dimensional changes due to differences in thermal coefficients of expansion between propellant and steel.

Numerous attempts were made to coat the steel with a relatively thick layer (1/16"-1/8") of a material which would adhere strongly to both the steel and the propellant and which would be capable of absorbing the above mentioned dimensional changes. Among the materials tried were

    25-75 Ethyl cellulose-Castor Oil
    35-65 Ethyl cellulose-Dutrex 25
    E.C.260-A degraded rubber
    E.C.711-A Neoprene rubber
    Cardolite 5185-A rubbery resin.

The first two were applied from the molten state, the others from solution. These failed with thermosetting propellants based on ZV5273 and on Cardolite 708-Furfural. Burning down the interface between propellant and liner occurred, apparently due to inability of a thin layer of liner to absorb dimensional changes.

Instead of bonding the liner to the steel motor walls, attempts
were made to prevent adhesion and thus to allow the liner to
adhere only to the propellant. The need for the liner to
absorb dimensional changes would thereby be eliminated. The
motor walls were coated with a film of Nujol or soap-glycerin
mixture, Ethyl Cellulose-Castor Oil liner applied and a
ZV5273 propellant cast into the motor thus prepared. 25% of
the shots were blows resulting from failure of the films to
prevent adhesion of the liner to steel or from flames
penetrating the liner. When a layer of 1/16" cork was used
in place of the oily film and the butt joint was left unsealed,
63% failures occurred at the cork joint. Sealing the joint
with cement reduced the number of failures to 14%. When an
overlapped joint, sealed with cement was used failures still
occurred to the extent of about 10%.

Since no material was available with the combination of
properties desired and since simple schemes to remove the
need for certain of these properties failed, little more
work along these lines was done. The possibility of using
a seamless flexible cup, made from rubber, which would fit
snugly against the inside of the motor has been considered.
If the propellant were capable of bonding tightly to rubber,
such a restriction would seem to be foolproof. Our materials
do not bond well to rubber and so we have done no experi-
mental work with such a scheme.