WADC TECHNICAL REPORT 59-338

PART III

Cleared November 2nd, 1972
Clearing Authority: Air Force Materials Laboratory

COMPOSITE INORGANIC RESILIENT SEAL MATERIALS

L. L. Smith

Armour Research Foundation

MARCH 1961

Materials Central
Contract No. AF 33(616)-5793
Project No. 8128

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

500 – June 1961 – 31-1170

FOREWORD

This report was prepared by the Armour Research Foundation of Illinois Institute of Technology under USAF Contract No. AF 33(616)-5793, Supplemental Agreement No. 2(60-254). This contract was initiated under Project No. 8128, "Transmission Technology", Task No. 73027, "Power System Associated Materials". The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. Roger E. Headrick acting as project engineer.

This report covers work conducted from March 1960 to February 1961.

During this work period, Quarterly Progress Report Nos. 6, 7, and 8 were issued. All essential information contained in the Quarterly Reports is included in this report.

Principal Armour Research personnel who have cooperated in the research effort and preparation of this report are: J. A. Fitzgerald, F. Iwatsuki (Supervisor), E. Nielsen, R.D. Noble, T.C. Parada, N. Parikh, M. Sabanas, L. L. Smith (Project Engineer), and T.S. Tully.

Data on this project are recorded in Armour Research Foundation Logbooks C-9514 and C-10270.

ABSTRACT

The principal objective of this research program is to investigate and develop composite materials suitable for use as static and dynamic seals at temperatures ranging from cryogenic to 1200°F and pressures up to 5000 psi.

Materials investigated may be grouped as follows:

1. Fibrous composites with pure metal impregnants. An example is stainless steel fiber skeletons impregnated with silver and/or indium with which promising results have been obtained at temperatures of 1000°F for reciprocating shaft seals and -424°F for static seals.

2. Fibrous composites with other impregnants. Included are metal skeletons filled with teflon, silicone, inorganic rubber, and various ceramic compositions.

3. Non-fibrous composites. These consist of ceramic composites containing talc or glass.

Included are studies of resilience, fiber orientation, friction and wear, static seals, reciprocating shaft seals, rotating shaft seals, and radiation effects.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

JmKelble

J. M. Kelble, Chief
Elastomers and Coatings Branch
Non-Metallic Materials Laboratory
Materials Central

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

LIST OF TABLES

LIST OF TABLES (Cont'd)

I. INTRODUCTION

This report covers work done under an extension to Contract No. AF 33(616)-5793 and is Part III of WADC Technical Report 59-338. It represents a continuation of the work summarized in Parts I and II, published in May and December 1959, respectively. While the desired temperature resistance in Parts I and II was room temperature to 1000°F, the desideratum has been broadened to cryogenic to 1200°F for this part.

Some of the materials discussed in this part are stainless steel and molybdenum skeletons, impregnated with silver, indium, tin, and various polymers and ceramics. The development and evaluation of these materials are directed toward static seal, rotating shaft seal, and reciprocating seal applications.

Included in this report, summarizing Quarterly Progress Report Nos. 6, 7, and 8, are the following topics: evaluation by outside organizations, three types of composites (fibrous with pure metal impregnants, fibrous with other impregnants and non-fibrous), sealing studies, and the effect of nuclear radiation on the more promising materials.

A seal material for use at high pressure and temperatures ranging from near absolute zero to 1200°F requires an unusual array of properties. Some of the metallic and refractory materials meet the high temperature requirements, but their other mechanical properties make them inadequate for seals. On the other hand, some materials like elastomers and rubber possess desired mechanical properties such as resilience and conformability at low temperatures, but are not serviceable at high temperatures.

Temperature is believed to be a more basic factor in the evaluation of seal materials since all engineering materials exhibit similar effects as the temperature is varied, namely, contraction and expansion, hardening and softening. Moreover, materials for dynamic seals must have resilience and suitable frictional properties.

Studies of various material fabrication techniques indicated that it would be possible to make composite material combinations which utilize the properties of the constituents and may eventually meet the requirements for seals.

Typical of the approach being taken are composite materials which begin as stainless steel or molybdenum fibers felted and bonded into a skeleton of desired shape and size. These skeletons are then filled with a second softer material to give two completely interpenetrating continuous

---

Manuscript released by author February, 1961 for publication as a WADD Technical Report.

phases. Since both phases are continuous, such a configuration offers an optimum possibility of combining the properties of each in the resultant material. Thus, a continuous rigid phase such as stainless steel or molybdenum offers maximum support to a continuous conformable phase of fillers.

There are two conditions which must be satisfied if a seal is to be leakproof. First, an initial seal must be formed at room temperature. Second, the initial seal must be maintained when the environmental temperature is raised or lowered under operating conditions. The operating conditions as applied to the seal involve a fluid medium, temperature, shaft speed, vibrations encountered, and the length of time that the seal can function under these conditions.

The study of sealing mechanisms and the conditions outlined above indicated that, for successful seal applications, materials should possess at least two basic properties, namely, resilience and temperature resistance. The other properties can be balanced by a compromise in design arrangement or changes of seal geometrical configuration. Therefore, experimental work was geared to produce composite materials and constituents for such compositions keeping in mind these basic property requirements.

The production of a material which would preserve its properties throughout the temperature range from near absolute zero to 1200°F, and would be suitable for static and dynamic sealing, is not easily fulfilled. However, some of the composite combinations showed excellent ability to serve as static seals at high temperatures. They were evaluated to serve as dynamic seals with some success. Different combinations were made for evaluation at low temperatures.

II. EVALUATION BY OUTSIDE ORGANIZATIONS

Two organizations have cooperated with Armour in operating full scale tests using ARF metal composite materials. Republic Aviation Corporation of Farmingdale, Long Island, New York, conducted reciprocating rod tests at high temperatures, while the Cryogenic Engineering Laboratory of the National Bureau of Standards at Boulder, Colorado, conducted static tests at low temperatures.

A. Republic Aviation

In a program to develop a hydraulic system to operate at about 4000 psi and 1000 °F, a number of seal configurations were fabricated by Republic from ARF composite material and evaluated in a full scale rig utilizing a reciprocating piston rod. The results are summarized in Table 1, and "indicate that seals fabricated from the ARF composite material show the most promise for 1000°F operation", according to Republic. Although the table shows that leakage occurred after as much as 115,000 reciprocation cycles in some cases, the performance of the

Table 1

SUMMARY OF DYNAMIC TEST RESULTS

1000°F SEAL DEVELOPMENT AT REPUBLIC AVIATION[1]

Republic Test No.	Seal Config.	Total Cycles	Cycles and Max. Temp.	Total Elapsed Time (hr)	Elapsed Time and Max. Temp. (hr)	Total Thermal Cycles	Remarks
173	Wedge Seal (ARF Composite)[2]	114,705	65,979 (900-1000°F)	30.5	17 (900-1000°F)	5	Rod seal leaked excessively while heating up during 6th thermal cycle
174	Same as above	36,145	11,482 (900-1000°F)	10.5	3.5 (900-1000°F)		Rod seal leaked excessively due to loss of squeeze caused by expansion of seal tension ring
176	Ring Seal (ARF Composite)[2]	54,813	34,853 (900-1000°F)	19.0	10	3	Static seal failed-replaced static. Dynamic seal leaked after reassembly
178	Pressure Energized Rod Seal (ARF Composite)[3]	32,935	--	13	--		Seal leaked excessively at 570°F

---

[1] From Bi-monthly Report No. 2, Phase III, Republic Aviation Project RAC 695-602 (113).

[2] No. 430 stainless steel - silver indium composite material

[3] Molybdenum fiber skeleton in silver matrix.

seals was superior to that of seals from other sources, which developed excessive leakage before 15,000 cycles.

B. National Bureau of Standards

It is reported elsewhere in this report that composites which have low melting temperature impregnants (like indium and tin) cannot retain pressures at high environmental temperatures in seal applications because the melted impregnant is forced out of the skeleton. These composites, however, may be useful as seals at low cryogenic temperatures, or for some other applications.

On this basis, four different composite combinations were prepared and sent to NBS Cryogenic Engineering Laboratory, Boulder, Colorado, for evaluation at cryogenic temperatures. They are identified as follows:

1. 430 stainless steel bonded fibers, 23 per cent skeleton density, impregnated with silicone resin slurry, a G.E. product designated as SR 32
2. 430 stainless steel bonded fibers, 23 per cent skeleton density, impregnated with indium
3. 304 stainless steel bonded fibers, 22 per cent skeleton density, impregnated with indium
4. Molybdenum unbonded fibers, 31 per cent skeleton density, impregnated with silver

The specimens were machined to fit their existing fixtures for experiments in which they were used as flat gaskets, and in thermal expansion and compression-recovery experiments. A photograph of three of these specimens is shown in Fig. 1, in which the short cylinder is intended for the compression-recovery experiments. The data available to date relate to the gaskets and are presented in Table 2.

The only samples which remained leaktight were those containing indium. Therefore it was concluded by NBS that indium impregnated stainless steel mesh makes good low temperature seals if confined (as in the case of the reported tests) and subjected to adequate initial sealing forces. The same was found by NBS in these tests to be true, however, for pure indium, so that the advantage of the stainless steel reinforcement remains to be determined. Since the supply of the hand-made gaskets was limited, it was not possible to test the indium-SS gaskets under other initial loads or unconfined conditions.

Figure 2 is a photograph of four of the gaskets, taken after the test. The captions are keyed to the NBS test numbers in Table 2. The scratches were incurred in removing the gaskets from the grooves in which they were stuck. It is noteworthy that the gasket with the silicone resin filler has recovered the most, and the pure indium gasket has

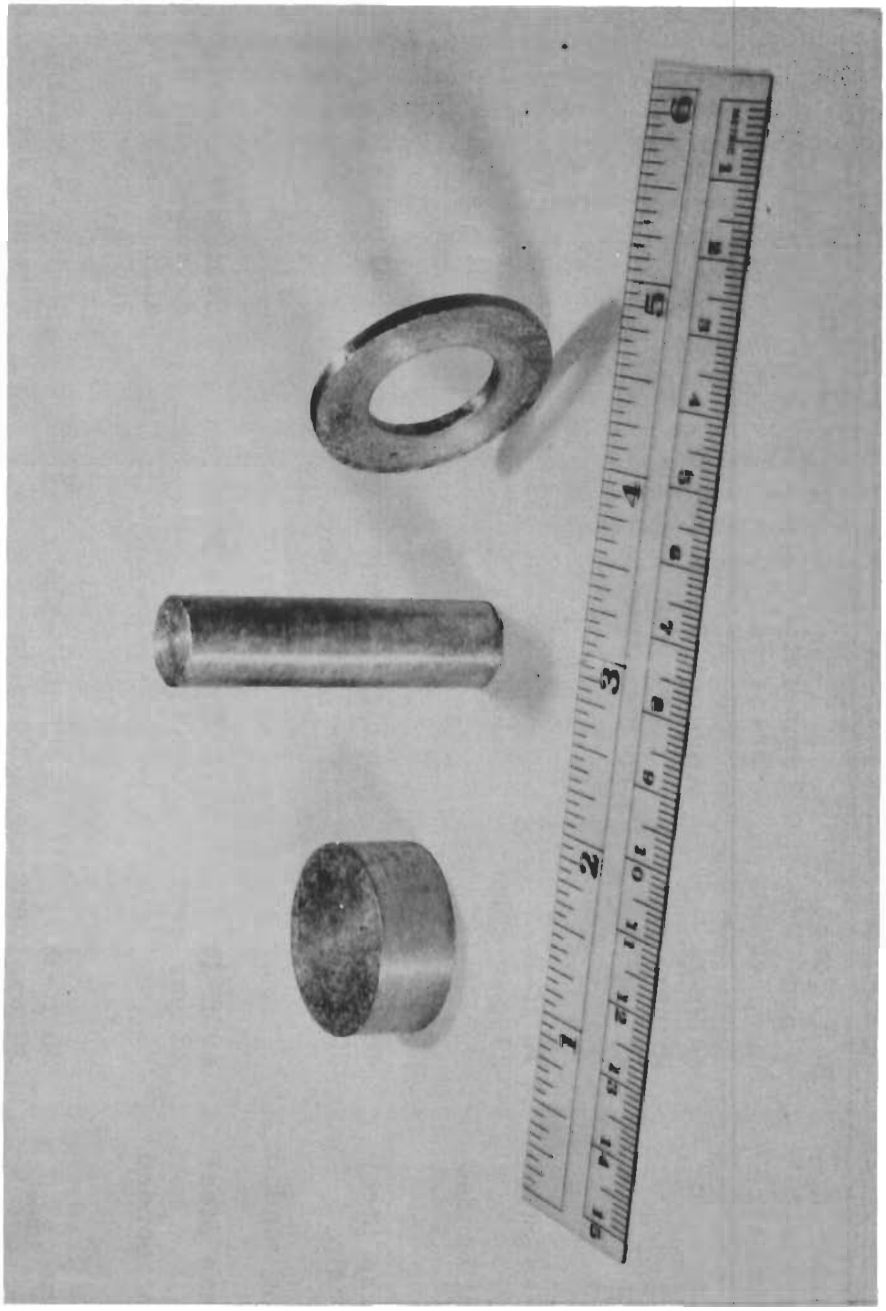


Fig. 1 COMPOSITE SPECIMENS FOR EVALUATION AT CRYOGENIC TEMPERATURES

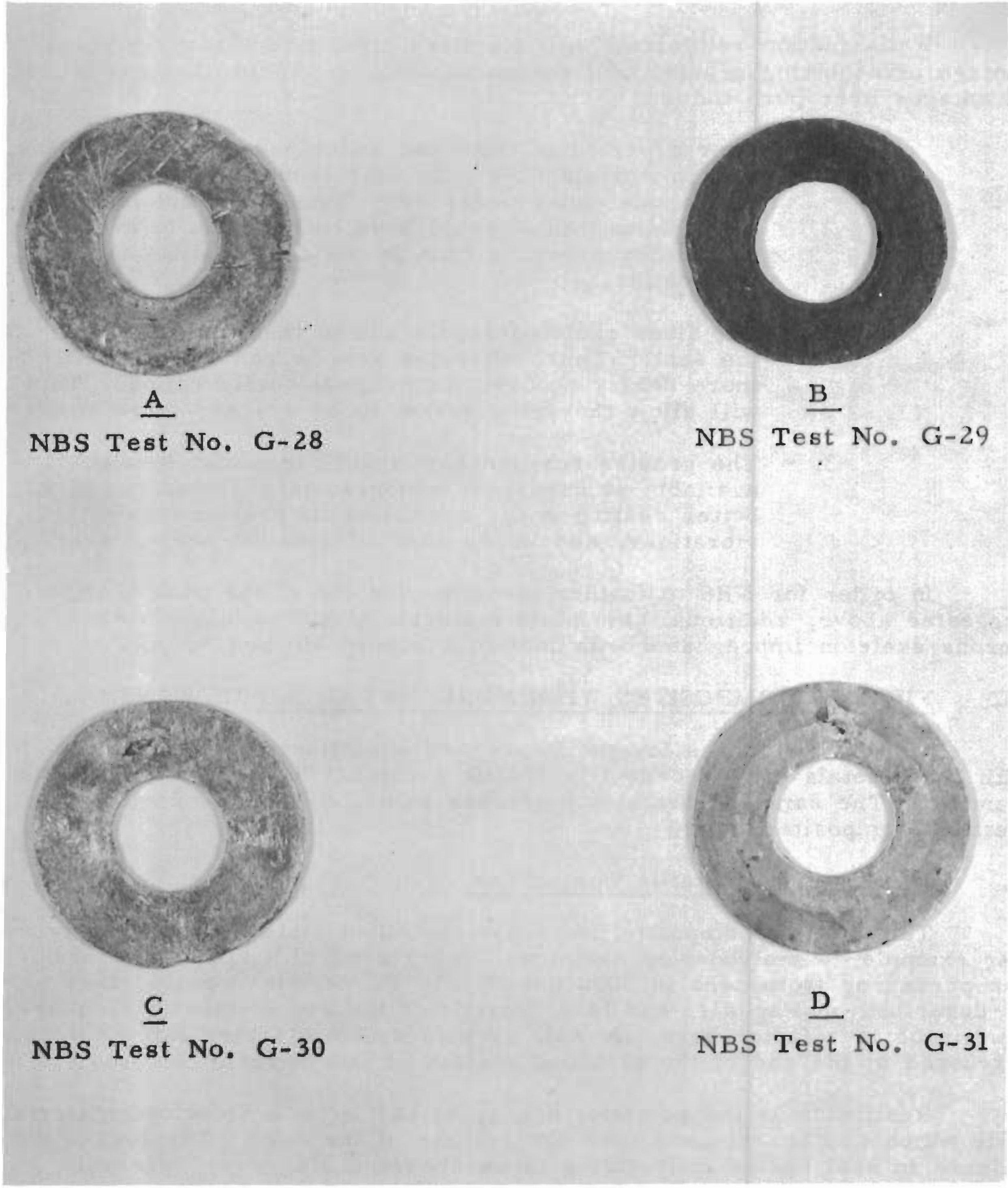
Table 2

SUMMARY OF STATIC TEST RESULTS CRYOGENIC SEAL DEVELOPMENT AT THE NATIONAL BUREAU OF STANDARDS[1]

NBS Test No.	Skeleton Material, Impregnant and Skeleton Density	Bolt Torque and Compression	Temperature and Pressure	Remarks
G-27	Molybdenum Silver 31 per cent unbonded	40 ft-lb 15 per cent	Ambient Temperature. High vacuum outside 500 psig inside	Seal failed
G-28	304 Stainless Steel Indium 22 per cent bonded	40 ft-lb 29 per cent	-323°F 1000 psig	Seal was leaktight. Indium extruded into clearance space. Test jig failure prevented testing to -424°F
G-29	430 Stainless Steel Silicone Resin Slurry 23 per cent bonded	40 ft-lb 30 per cent	Ambient Temperature. 10^{-5} mm Hg vac.	Seal failed
G-30	430 Stainless Steel Indium 23 per cent bonded	40 ft-lb 28 per cent	72°F to -424°F 1000 psig	Seal was leaktight. Indium extruded into 0.001 in. clearance space between tongue and groove.
G-31	Pure Indium	20 ft-lb 30 per cent	72°F to -424°F 1000 psig	Seal was leaktight. Indium extruded into clearance space.

---

[1] From NBS Monthly Progress Report of October 30, 1960, to Boeing Aircraft



A
NBS Test No. G-28

B
NBS Test No. G-29

C
NBS Test No. G-30

D
NBS Test No. G-31

Fig. 2 GASKETS AFTER EVALUATION AT NBS

recovered the least, judging from the outside diameters and thicknesses.

While indium reinforced with stainless steel fibers has the disadvantage of requiring greater bolt torque to seal, it should have the following advantages over pure indium:

1. Over a period of time and under unconfined conditions, pure materials have a greater tendency to relax, creep, or extrude under pressure. Thus, to avoid leakage, more adjustments would have to be made to keep the seal under pressure than in the case of fibrous composites.

2. The fiber skeleton should add to the resilience of the seal. Thus, when the seal is removed, it will more nearly recover its original configuration. This will allow the same gasket to be re-used more times.

3. The greater resilience of the fiber skeleton seal, if available at cryogenic temperatures, should result in better sealing under conditions of pressure pulsations, vibrations, and in the case of dynamic seals, wear.

In order for NBS to further investigate some of the possibilities suggested above, additional composite material of 316 stainless steel fibrous skeleton impregnated with indium has been shipped by ARF.

III. FIBROUS COMPOSITES WITH PURE METAL IMPREGNANTS

Melting techniques for the impregnation of fiber metal skeletons with pure metals are described in WADD Technical Report 59-338, Parts I and II. The same report also discusses many physical properties of metallic composites.

A. Resilience of Metallic Composites

This type of composite has shown excellent static sealing ability. For example, a molybdenum skeleton impregnated with silver retained gas pressures from zero to 5000 psi at 1200°F, despite repeated cycling, as described on Pages 13 and 14 of Part II of the report mentioned above. Resilience is a factor here, as well as with dynamic seals, for the reasons discussed at the end of the previous section of this report.

Resilience is the potential energy stored up in a deformed material body which can be released upon the release of the load. The load release in seal bodies and sealing faces occurs during wear, pressure pulsations, and vibrations. If the seal material has no resilience, one or all of the above conditions will cause a loss of pressure on the sealing surfaces, and excessive leakage results.

The resilience modulus is equal to the work required to deform the body from zero stress to the stress approaching the elastic limit. Stress and strain values needed for resilience modulus determination are measured on standard size specimens adapted by ASTM for this purpose. These standard size specimens, however, are not suitable for the determination of the resilience of composite materials. First, metallic composites with which we are experimenting do not have a clearly defined yield point, and the line on the stress-strain graph is a curve instead of a straight line as obtained with solid metallic materials. Secondly, we are interested in strain values up to 10 per cent of the original specimen length at which the yield point is partially exceeded and most of the metal fibers are plastically deformed.

To establish a yardstick for the comparison of resilience properties of various composite materials, specimens 1/2-inch diameter and 3/4-inch long were made.

Composites whose resilience properties were studied are designated by number and their constituent percentages are listed below:

2.[1] 430 stainless steel unbonded fibers, 27 per cent skeleton density, impregnated with tin

3. 430 stainless steel bonded fibers, 27 per cent skeleton density, impregnated with tin

4. Molybdenum unbonded fibers, 18.5 per cent skeleton density, impregnated with tin

5. Molybdenum unbonded fibers, 59 per cent skeleton density, impregnated with indium

6. 430 stainless steel bonded fibers, 39 per cent skeleton density, impregnated with tin

7. Molybdenum unbonded fibers, 40 per cent skeleton density, impregnated with silver

8. 430 stainless steel bonded fibers, 73 per cent skeleton density, impregnated with tin

9. 430 stainless steel bonded fibers, 27 per cent skeleton density, impregnated with magnesium

---

[1] These are the same composite numbers designated in the Part I and Part II summary reports.

Experimental data are shown graphically in Figs. 3, 4, 5, and 6. The data consist mainly of stress-strain and percentage recovery values recorded when specimens were compressed to 1, 2, 5, and 10 per cent of their original lengths, and also when repeated compressions equal to approximately 1 per cent of their original lengths were made.

Figure 3 shows that, even after deformations reach 10 per cent of their original length, some energy is left for partial recovery upon the release of the load. This is attributed to the nature of the basic fiber network body - its density, bonding, and the kind of impregnant that is used to fill skeleton pores. When the load is applied, some of the randomly located fibers are stressed first, and as the deformation increases the other fibers begin to be stressed. In the meantime, the first fibers surpass their yield points, become plastically deformed, and the energy thus expended is not recoverable.

Figure 4 shows an increasing percentage of recovery after repeated small deformations. This was expected and is due to the work hardening of composite fibers.

Figure 5 indicates that higher stresses are needed to compress composites having denser skeletons and impregnants with a high modulus of elasticity.

Figure 6 shows the stress increase for the same amount of repeated strain. Only Composite No. 8 indicated a stress decrease. This may be due to the very dense skeleton (73 per cent). To verify this behavior, additional experiments should be performed.

It was concluded that metallic composites possess a large amount of resilience. Some recovery was obtained even after 10 per cent deformation. A much larger percentage of recovery is expected with polymeric impregnants, and the same deformation will be reached with smaller loads.

B. Fiber Orientation Study

New experimental results indicate that the mechanical properties of composite metals or alloys exhibit a dependence upon the direction from which the test samples are obtained. Initial tests indicated that if the samples are cut so the compressive test force is applied at right angles to the direction of felting (diameter direction, as shown in Fig. 7) the recovery properties are improved.

In the initial tests it was found that samples cut from the composites of fiber-metal alloys in the axial direction show virtually no reinforcement while those cut from the diameter direction exhibit improvements in mechanical properties proportional to the fiber concentration. This being the case, it was thought that the resiliency of such composites may also be orientation dependent.

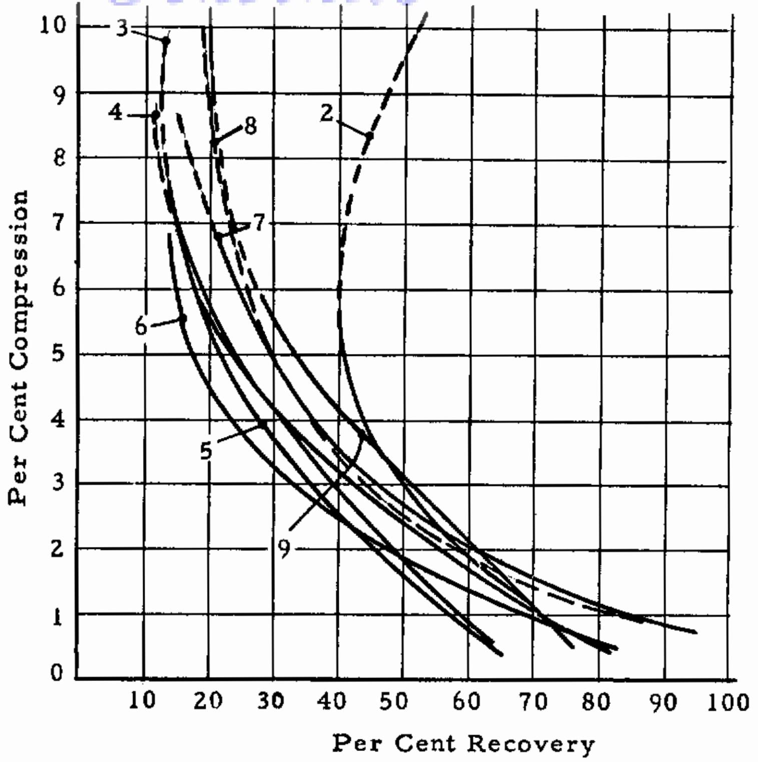


Fig. 3 LARGE DEFORMATIONS AND RECOVERY

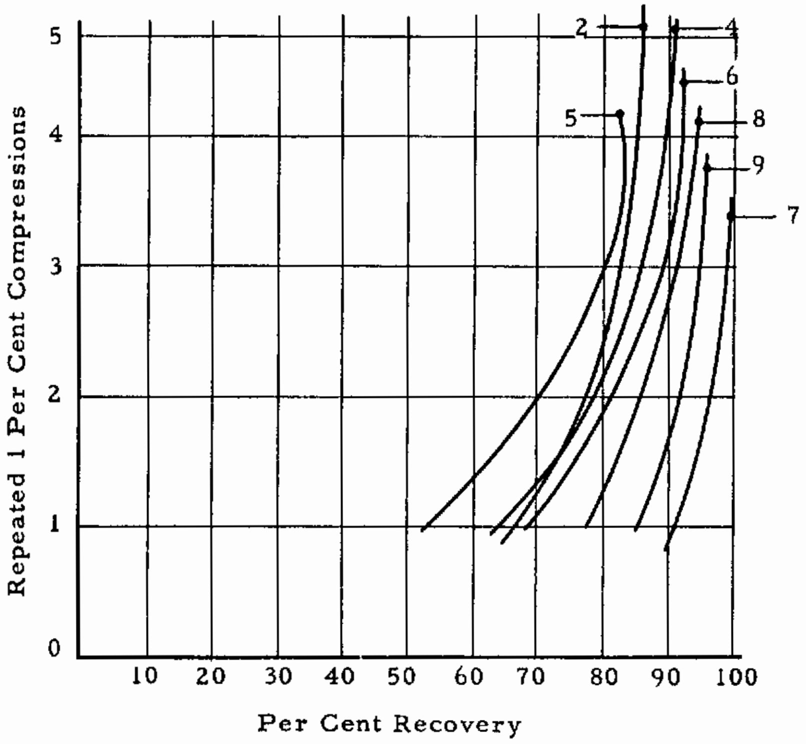


Fig. 4 REPEATED SMALL DEFORMATIONS AND RECOVERY

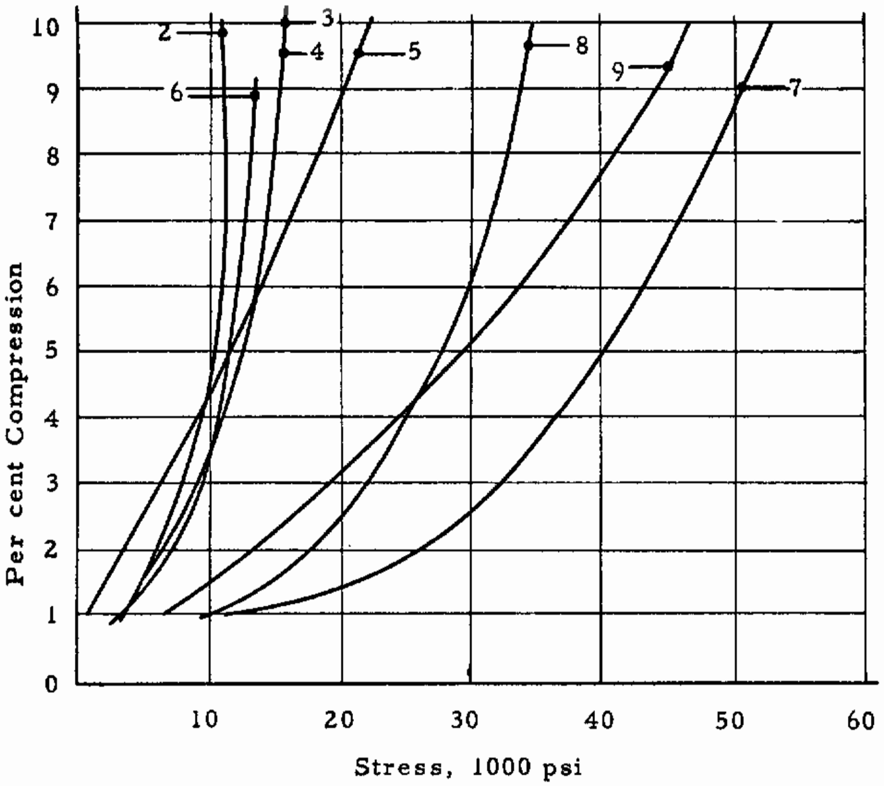


Fig. 5 STRESS REQUIRED FOR LARGE DEFORMATIONS

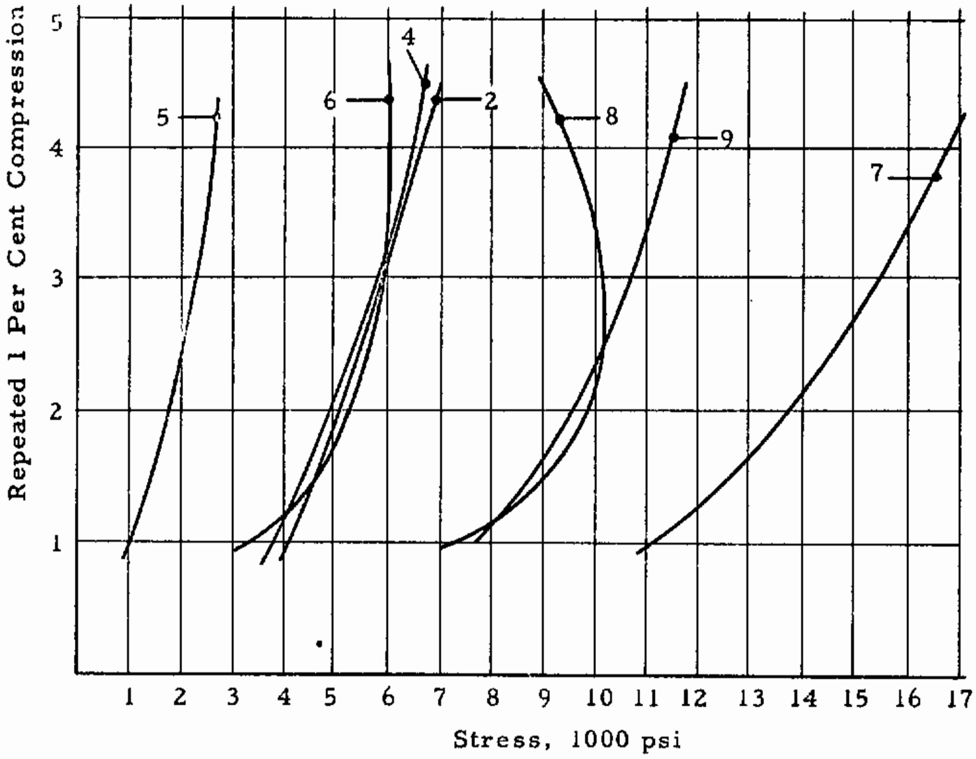


Fig. 6 STRESS REQUIRED FOR REPEATED SMALL DEFORMATIONS

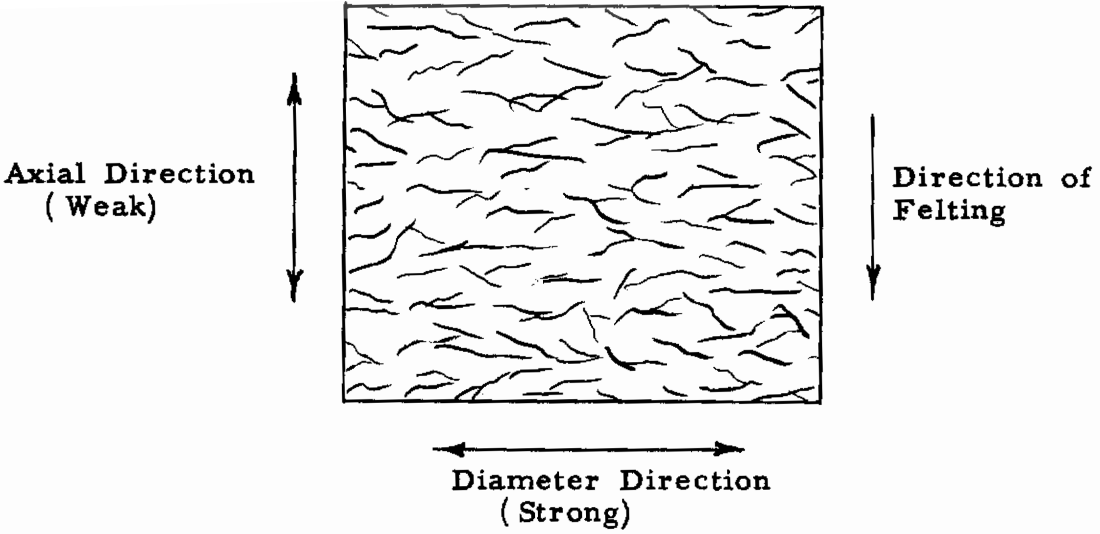


Fig. 7 CROSS-SECTION OF FELT

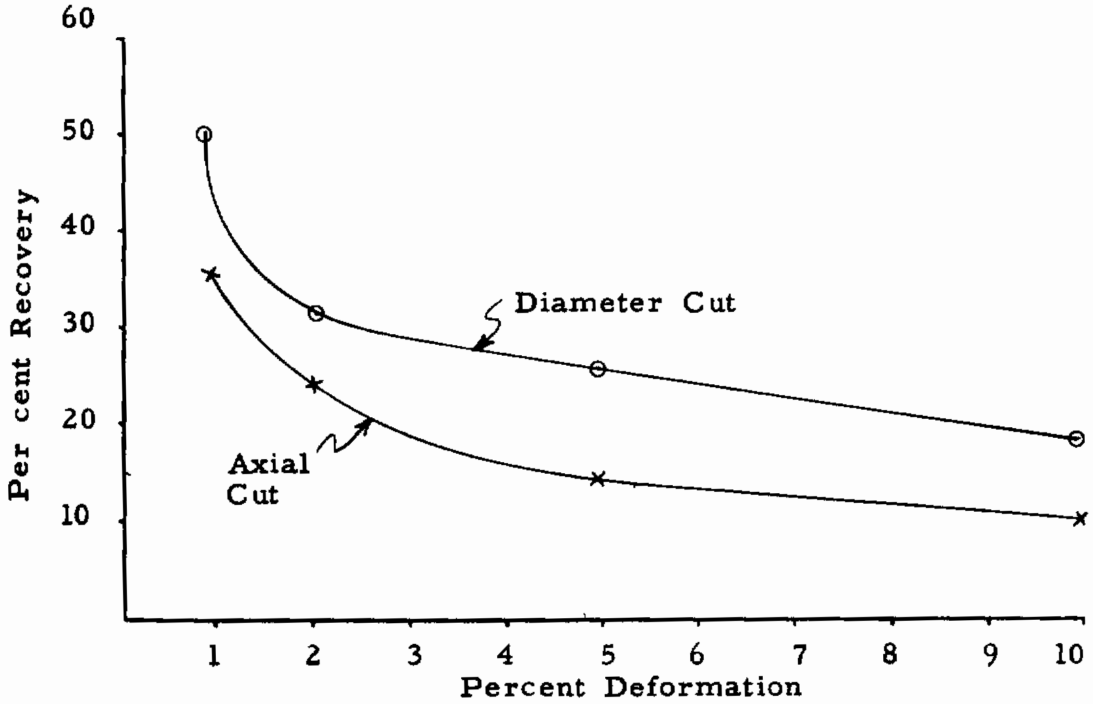


Fig. 8 RECOVERY OF AXIAL AND DIAMETER CUT SAMPLES OF COMPOSITE

To test this theory, a large sample was prepared by impregnating molybdenum fibers with silver. The samples contained 25 per cent molybdenum fibers by volume and were 2-1/2 inches in diameter and 3 inches long. Test pieces (1 inch in diameter by 1 inch long) were cut from axial as well as diameter directions.

In Fig. 8, per cent recovery is plotted against deformation for the two specimens. The graph shows a consistent improvement in recovery of the diameter cut sample over the axial cut sample. Future specimens for evaluation by Republic Aviation and the National Bureau of Standards should be cut in both directions to determine the differences in full scale applications.

C. Metallic Fillers

Fiber metal structures provide mechanically strong and resilient bodies. For use as seals, such material bodies have to be impregnated with other materials to eliminate porosity, to obtain soft conformable sealing surfaces, and to impart self-lubricating properties.

The selection of fillers is limited to materials which are known to have reasonable thermal stability. One suitable type of filler is metallic.

In addition to the metallic fillers already reported, alloys consisting of silver and indium were prepared and used as fillers. It is believed that alloying of silver and indium, with the corresponding drop in the solidus temperatures, should result in substantial changes in strength and resiliency of the composites. The criterion governing the selection of alloy systems for impregnation was the availability of the Ag-In Phase Diagram which shows that the addition of 16 per cent indium to silver lowers the alloy solidification temperature. It also gives reasonable assurance that this amount of indium will dissolve completely and a single phase of solid solution will be formed as the alloy cools.

The alloys were melted in different atmospheres in order to obtain sound ingots. Only a very cursory examination of these alloys has been completed. No mechanical tests were conducted on the samples since it was decided to perform field tests first. However, the investigation has yielded sufficient information so that one can selectively impregnate fiber metal felts with those alloys which can be prepared in the laboratory without great difficulty.

Samples have been supplied to Republic Aviation Company for evaluation as dynamic seals to seal a reciprocating shaft, as discussed in an earlier part of this report.

Some of the relevant properties of the alloys are listed in Table 3.

Table 3

ALLOY COMPOSITIONS FOR USE AS IMPREGNANTS

Number	Atmosphere	Solvent	Solute, Per cent	Hardness, BN	Solidus Temp., °F	Remarks
1	Vacuum	Ag	16 In	36.8	1400	Good
2	Vacuum	Ag	10 In		1540	Good
3	Argon	Mg	10 In	32.4	1130	Slight reaction with steel crucible
4	Argon	Mg	20 In	33.6	1080	Reacts with Vycor
5	Argon	Mg	30 In	34.4	1020	Reacts with Vycor
6	Argon	Ag	18 Zn		1360	
7	Argon	Ag	1.5 Li	27.8	1400	
8	Argon	Ag	32 Hg		1300	

Several composite combinations containing metallic fillers are shown in Fig. 9. A specimen is shown in which the filler was extruded from the felt when the environmental temperature reached the melting point of the filler metal.

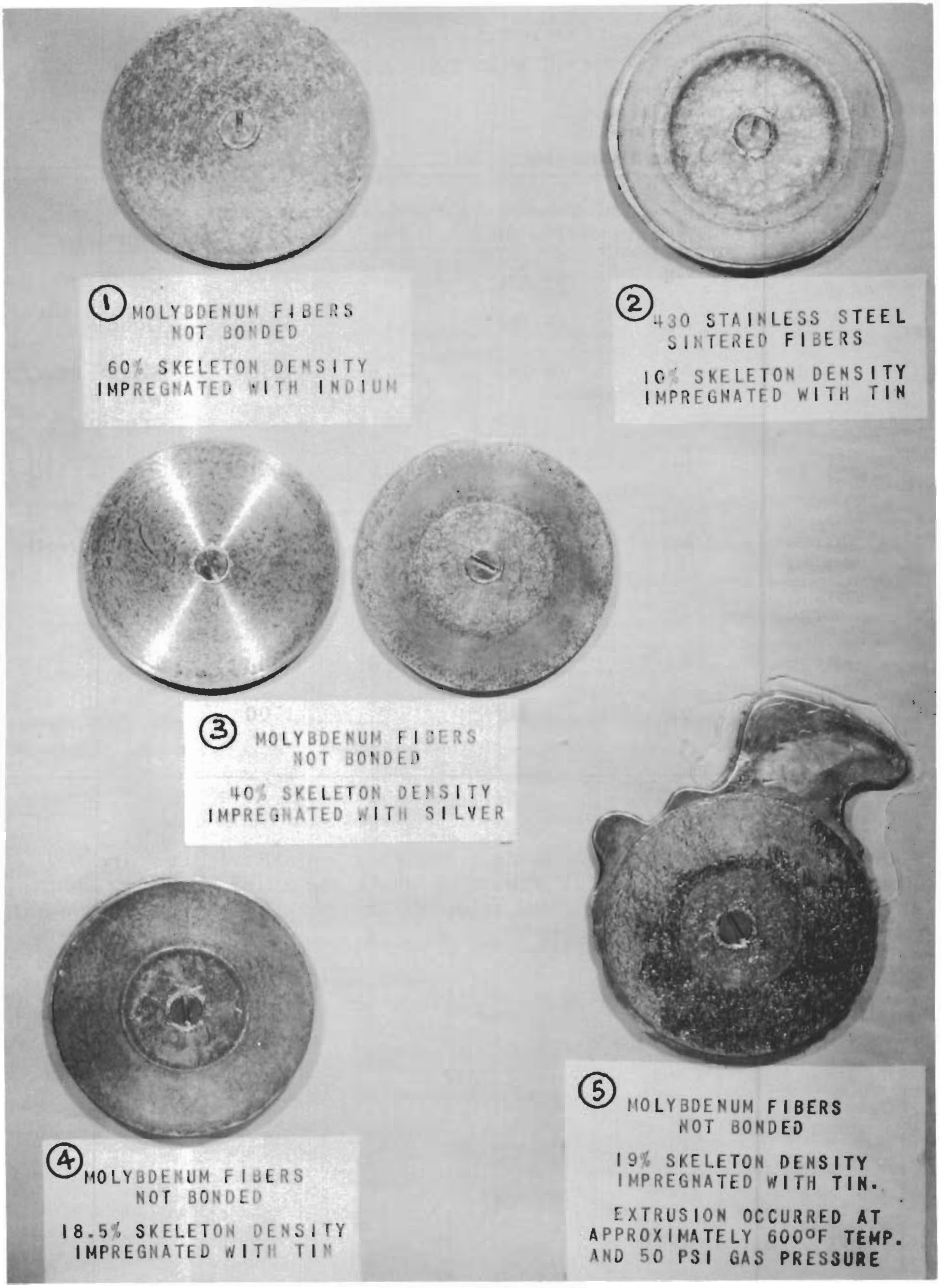


Fig. 9 COMPOSITE SPECIMENS IMPREGNATED WITH METALLIC FIBERS

D. Metallic Coatings

A need exists for a low pressure seal for pressures up to about 15 psi and for temperatures of 1200°F or higher. Such seals would be useful as gaskets for space vehicles and similar applications. For this type of seal it would be advantageous to have a material which would require less clamping force than present composite materials.

For this application it appears worthwhile to investigate the combination of a skeleton (unfilled or partially filled) with a coating such as silver. Beside the lower bolt torque which may be needed, such a seal would have a further advantage over usual composites in that less silver would be required.

The following may be disadvantages of this construction:

1. The possibility of the fiber ends piercing the coating when clamped, such as occurred with silver foil in a static test discussed under Static Seal Evaluation.
2. The possibility that a coated skeleton will be crushed when sufficient compressive forces are applied to the coating to effect a seal.
3. The possibility that the coating may creep or extrude at elevated temperatures because there are no fiber ends present in the coating to restrain it.
4. As indicated elsewhere in this report, the bare metal skeleton requires a much greater force to compress than is needed by most elastomers. However, this may be the penalty exacted to obtain greater temperature resistance.

Following are some of the methods which can be used to place a coating on the surface of the skeleton:

1. Electrolytic plating
2. Vacuum deposition
3. Spinning of a shell
4. Machining of a shell
5. Flame spraying
6. Dipping in melt
7. Melting of powder on surface
8. Painting with fine powder dispersed in a vehicle

It is necessary, for all of these methods to be successful, to start with a finished skeleton surface. For methods 1 and 2 this surface should also be non-porous for the coating to be non-porous. For methods 3 and 4 a sufficiently finished surface is required to avoid piercing the coating with the fiber ends. For methods 5 through 8 also, an irregular coated surface may result unless the base surface is properly finished.

For this reason, first priority in this study was given to obtaining a finished surface. The approach tried was grinding. The first specimens on which this was tried were stainless steel skeletons impregnated with talc-potassium silicate. On contact with a No. 46 grinding wheel, the samples became quite hot, and the surface appeared to partially fuse. A glossy, continuous layer formed on the surface. When tested without a coating, such samples were found still to be permeable to low pressure air and to provide a seal no better than already demonstrated for the talc-potassium silicate impregnation.

Samples of bare stainless steel skeleton with 2 inch diameter surfaces were put on a surface grinder and ground smooth in attempting to get a non-porous surface. Upon inspection after grinding, most of the original voids were still observed. Other samples were tried with less surface in contact with the grinding wheel and with more force applied. Surfaces with less voids resulted, and it appeared that local melting of the fiber ends had occurred.

Simple experiments were performed using method 8 listed above. First, free flowing silver powder was vibrated into the structure and then an overcoating of silver paint was applied. The resulting gaskets were very porous and no seal was obtained up to maximum compression.

E. Friction and Wear Studies

The procedure and apparatus used to evaluate friction and wear is described in Appendix I. Briefly, an impregnated skeleton sample of 1/4-inch diameter and 3/8-inch length was inserted as a snug fit in a spring loaded holder. The circular face of the sample was brought into full contact with a smoothly ground stainless steel (304) mating surface. A compression of 4 pounds (about 80 psi) was maintained on the holder. The sample and mating surface were enclosed in an electric furnace and heated to 1200°F. When stable conditions were reached, rubbing of the plate against the stationary sample was started. The plate was reciprocated by an air cylinder with a 3-1/2-inch stroke. An average surface velocity of 55 ft/min was maintained. Each sample was evaluated for 5 minutes running time.

To measure wear, samples were weighed and their lengths were measured before and after testing. At the conclusion of each run, the air cylinder linkage was disconnected, and a calibrated spring scale was attached to the movable shaft. The minimum force required to pull the mating surface across the sample was determined and is reported as breakaway friction.

The performance of impregnated fiber metal skeletons is summarized in Table 4. For comparative purposes, wear and friction data are listed for a typical skeleton unimpregnated. For this sample, wear was rapid

Table 4

FRICTION AND WEAR CHARACTERISTICS OF METAL IMPREGNATED FIBER METAL SEALANTS

Sample No.	Composition	Sealant Weight Loss, per cent	Sealant Wear Rate, in/min	Break-away Friction, lb.	Remarks
1	430 SS, bonded 23 per cent skeleton density, no impregnation	0.80 wt. gain	0.004	5	Plate deeply scored. Sealant slight deformed.
2	430 SS, bonded 30 per cent skeleton density, impregnated with silver plus 16 wt. per cent indium	16.3	0.012	-	Plate scored; droplets of melted sealant scattered over plate.
		1.0	0.0007	-	Evaluation repeated but at lower temperature of 1000°F. Less damage to sealant resulted but scoring of plate continued.
3	304 SS, bonded, 22 per cent skeleton density, impregnated with indium	0.08	0.002	3	Temperature lowered to 300°F. Better operation resulted. Sealant was found to provide uniform deposit on plate.
4	Molybdenum fiber, not bonded, 31 per cent skeleton density, impregnated with silver.	near 0	+ 0.00008	3	Smooth operation. No perceptible scoring of plate.

Test Conditions: 1200°F
Rubbing Speed: 55 ft/min

Load on Sealant: 4 lb. (80 psi)
Running Time: 5 min.

and deep scoring of the mating plate occurred. Indium and silver-indium alloys were too low melting for use as impregnants in skeletons exposed to 1200°F. At lower temperatures, the lubricating effects of these materials were evident, particularly those of the silver-indium alloy. The lowest wear rate and the best performance was observed with a molybdenum fiber skeleton impregnated with silver.

IV. FIBROUS COMPOSITES WITH OTHER IMPREGNANTS

A. Polymer Impregnants

1. Teflon

Impregnation of a porous metal seal with a polymer will eliminate or minimize porosity for service temperatures up to the decomposition temperature for the polymer. If the polymer has the added feature of leaving a high residue upon decomposition by heat, serviceability may extend considerably beyond the decomposition temperature of the polymer.

The impregnation must be done without the aid of a solvent, since the removal of the solvent after impregnation will invariably give rise to porosity. The polymer must, of course, be of the thermosetting type. Therefore, suitable polymers are those for which liquid or fusible prepolymers can be made. After the seal has been impregnated, heat is applied to convert the polymer to the thermoset state. Both organic and semi-organic polymers can be considered for this purpose.

Attempts were made to impregnate metallic felts with a DuPont product designated as Teflon 30. Teflon 30 is an aqueous dispersion containing 60 per cent by weight of resin solids. It was included in this study because of its well-known low friction and lubricating characteristics and commercial availability.

Nearly all composites made with teflon filler were much too porous to retain gas pressures. When such composite structures were compressed, as is done in seal applications, the porosity was eliminated. However, the material became porous again when heated and progressively deteriorated with continued exposure to temperatures above 500°F.

2. Inorganic Rubber

Work with phosphonitrillic chloride, known as "inorganic rubber", was described in the Part II summary report but will be reviewed here. This polymer was prepared by producing and mixing crystals of the trimer $(PNCl_2)_3$ and the tetramer $(PNCL_2)_4$ and then applying a melt-impregnation technique. There is no serious void problem as with some other polymers because there is no solvent to evaporate.

As previously reported, two standard discs consisting of bonded 430 stainless steel fibers with 47 per cent skeleton density were impregnated with this polymer and subjected to a static seal evaluation. Gas pressures up to 5000 psi were retained at room temperatures. The temperature was then raised to approximately 820°F. After a two-hour exposure to this temperature, pressure cycling from zero to 5000 psi was applied. Slight leakage was noticed after 15 cycles. The maximum bolt torque was about 20 ft-lb for one disc and 47 ft -lb for the other disc. There was no bolt torque loss after cooling to room temperature.

However, despite these encouraging results, the polymer suffers from the following limitations:

1. The exposed seal surfaces are subject to hydrolysis in the presence of moisture.
2. The chlorine is corrosive to the metal skeleton.
3. The thermal stability should be improved.

Therefore, it was suggested that the surfaces be subjected to a chemical reaction which would remove the chlorine atoms from the surface layer and replace them with stable groups. This should help overcome all three of the above limitations.

With this objective in mind, seals (for configuration, see section on low pressure seals) made of 430 stainless steel, 23 per cent density, were divided into four groups treated as follows:

1. This group was impregnated with a melt composed primarily of the trimer, with some tetramer present. The impregnated seals were immersed for 10 minutes in a solution of KNH_2 in liquid ammonia for surface stabilization. This reaction for the trimer is typical:

$$(PNCL_2)_3 + 6\ KNH_2 \longrightarrow (PN(NH_2)_2)_3 + 6\ KCl$$

The $(NP(NH_2)_2)_3$ forms the outside layer of the seal and is stable.

2. For increased stability, this group was impregnated with a partially cyanolated phosphonitrillic chloride with a melting point of 80-90°C. This was followed by a 10-minute immersion in a solution KNH_3 in liquid ammonia for further stabilization of the surface.

3. Treatment of this group was the same as No. 2, except that the cyanolated phosphonitrillic chloride had a melting point of 93-103°C.

4. This group was treated the same as No. 2, except that the immersion in the KNH_2 solution was prolonged to 1/2 hour.

3. Silicone Resin

Several attempts were made to impregnate a metal fiber skeleton made of 430 stainless steel, 23 per cent density with silicone resin slurry designated as SR-32 (supplied by General Electric Company). This silicone resin is a viscous preparation containing 60 per cent solids by weight in toluene solvent.

The skeletons had a disc-like shape, the outside diameter was 2 inches, and the approximate thickness was 1/8-inch. Initially, these discs were simply soaked in the liquid silicone, then wiped off to remove excess material and transferred to an oven for curing. It was found that the skeletons were not thoroughly penetrated by slurry with this ordinary soaking. Next, the submersion in silicone was conducted in a vacuum chamber. Escape of air bubbles from the disc was noted, and apparently better penetration was obtained. Considerable quantities of entrapped silicone, however, dripped out before they could be hardened by heat curing. To minimize the dripping, rapid heating to set the resin was attempted. Blistering and expulsion of the resin from the disc body occurred. Repeated soaking under vacuum followed by heat curing failed to densify the skeleton. Voids were observed, and leakage of air at 5 psi persisted after three treatments.

B. Polymer-Ceramic Impregnants

Somewhat better retention of silicone was obtained by troweling talc powder into the surface of the skeleton before soaking. Repeated filling of surface holes with talc followed by silicone impregnation and curing occasionally provided a disc sample through which air would not flow at 60 psi pressure. Leakage, however, was rapid at 90 psi.

Attempts were made to fill all of the skeleton body with talc rather than merely entrap the powder in the surface irregularities. Vibration of the powder into the body was tried, but the talc persisted in packing at the surface.

Table 5 lists typical results of repeated impregnations with talc-silicone slurry, teflon dispersion, and concentrated aqueous solution of mono-aluminum phosphate. The subsequent impregnations were performed with a higher pressure differential in order to force additional slurry into the skeleton.

The highest composite density was obtained with silicone slurry. The skeleton impregnated with teflon appeared to be well filled, but could not retain air pressures over 40 psi.

Mono-aluminum phosphate did not densify the skeleton voids sufficiently. Air pressures over 10 psi could not be retained.

Few attempts were made to seal the skeleton glass. Powdered glass, such as lead borosilicate frit (Pemco 461), was troweled and pressed into the disc surfaces. The sample was then lightly oversprayed

Table 5

IMPREGNATION OF METAL FIBER SKELETON WITH NONMETALLIC FILLERS

Sample Number	Impregnant	Initial Sample Weight, grams	Weight after impregnation and curing 1st treat.	2nd treat	3rd treat.	4th treat	Remarks
1	talc-silicone slurry 55 per cent silicone 45 per cent talc	13.1019	19.0250	20.3270	20.4128		Some leakage through body with 90 psi air
2	aqueous teflon dispersion, 60 per cent solids	12.0515	16.9038	18.5728	20.2210	20.4203	Pressurized air forced soft teflon out of body
3	mono-aluminum phosphate liquor, 50 per cent concentration	13.9809	15.9108	16.9718	17.9155	18.0292	Leakage through body with only 10 lb pressure

with an aqueous slurry of the glass suspended in clay. After drying, the glass was fused with short heating at 1350°F. The molten glass was found to soak into the skeleton. Poorly filled voids were readily visible. Repeated applications of glass resulted in a build-up of badly pinholed deposits on the surfaces. Such structures were rigid and cracked with the slightest flexing. All were, of course, permeable to low pressure air.

Somewhat better sealing with glass was obtained by using either talc or alumina to fill surface voids. A thin application of glass slurry was sprayed over the treated surfaces. The samples were then dried and fuzed. Refractory fillers retarded the flow of molten glass into the body and provided a smooth, continuous surface coating. Samples were permeable to 40 lb air pressure. Attempts to recoat for greater sealing resulted in blistered porous deposits.

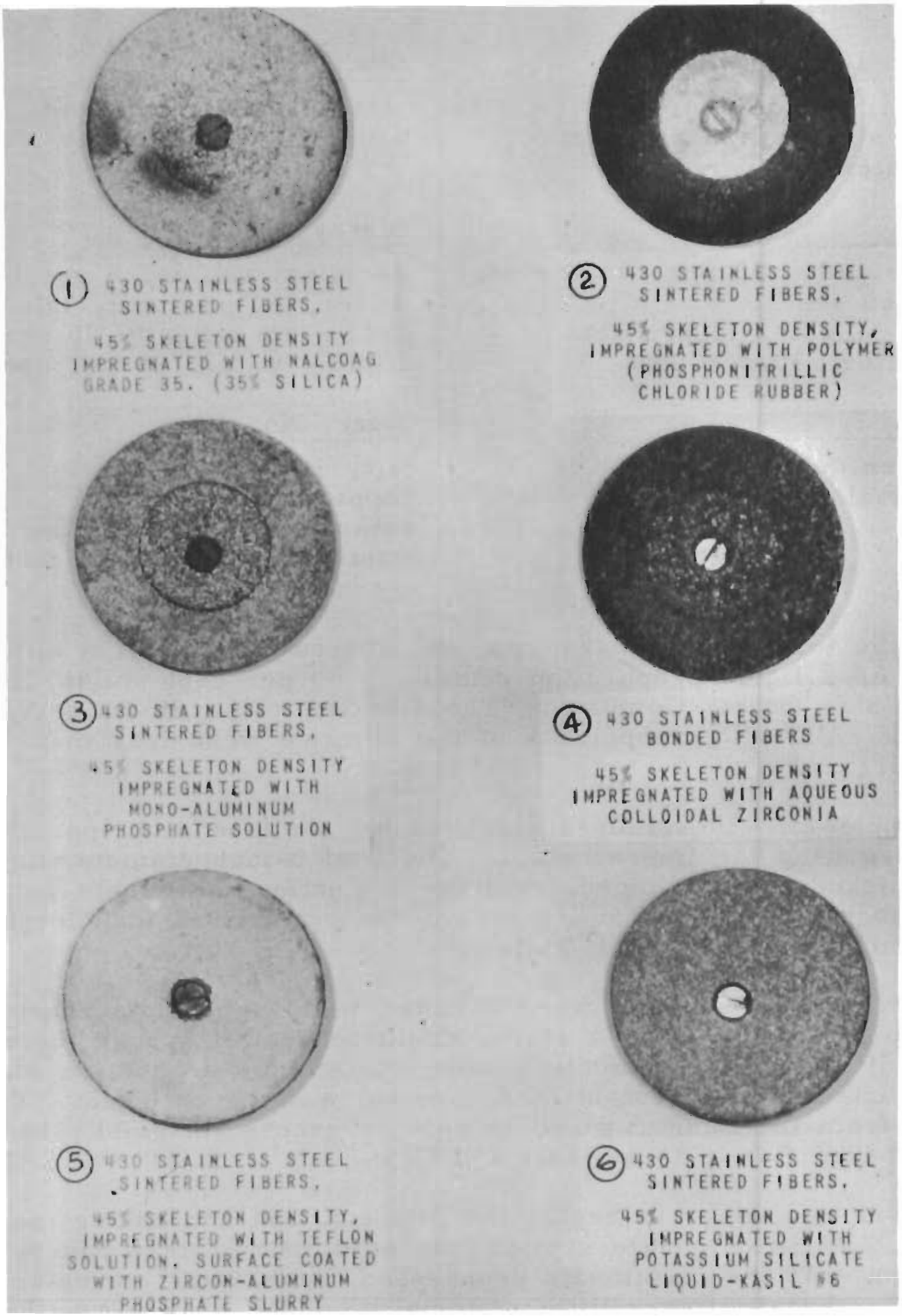
The leakage through the composite body at certain air pressures indicated in the remarks column of Table 5 was determined without any extra compacting or pressurization of the specimen. Small capillaries, allowing air passage at higher pressures, can be eliminated by pressurization. In actual seal applications, the material is always initially compressed. Since these composites possess highly desirable resilience properties and are moderately heat resistant, it is desirable to find out how they will function as actual seals.

Several composite combinations containing nonmetallic impregnants are shown in Fig. 10.

C. Preparation of Samples

Attempts were made to evaluate the wear properties of ceramic or refractory materials so that those with the best high temperature lubricating characteristics could be selected for use as impregnants in fiber metal skeletons. An objective was to fill the porous, compressible metal structures with thermally stable material to provide a wear resistant and pressure tight seal material. For contemplated operation of dynamic seals at 1200°F, comparative wear tests of a great number of composites indicated that the best lubrication can be expected with compositions containing silver, talc, cadmium sulfide, and copper.

Impregnation of the metal fiber structure with impregnants other than pure metals is accomplished best by drawing material into it such as by suction filtration. Slurries of the desired impregnating materials therefore were prepared. Composition of the slurries was based on the pressed composites of finely powdered solids and liquid binder as evaluated in the earlier friction studies. Generally, to obtain workable slurries, it was necessary only to add water to these relatively dry mixtures. Composition of the ceramic slurries along with a silicone preparation and the fibrous slurry received from Minnesota Mining are listed below. The Minnesota Mining material, as received, contains 2 per cent solids. Before use as an impregnant it was concentrated by



① 430 STAINLESS STEEL
SINTERED FIBERS,
45% SKELETON DENSITY
IMPREGNATED WITH NALCOAG
GRADE 35. (35% SILICA)

② 430 STAINLESS STEEL
SINTERED FIBERS,
45% SKELETON DENSITY,
IMPREGNATED WITH POLYMER
(PHOSPHONITRILLIC
CHLORIDE RUBBER)

③ 430 STAINLESS STEEL
SINTERED FIBERS,
45% SKELETON DENSITY
IMPREGNATED WITH
MONO-ALUMINUM
PHOSPHATE SOLUTION

④ 430 STAINLESS STEEL
BONDED FIBERS
45% SKELETON DENSITY
IMPREGNATED WITH AQUEOUS
COLLOIDAL ZIRCONIA

⑤ 430 STAINLESS STEEL
SINTERED FIBERS,
45% SKELETON DENSITY,
IMPREGNATED WITH TEFLON
SOLUTION. SURFACE COATED
WITH ZIRCON-ALUMINUM
PHOSPHATE SLURRY

⑥ 430 STAINLESS STEEL
SINTERED FIBERS,
45% SKELETON DENSITY
IMPREGNATED WITH
POTASSIUM SILICATE
LIQUID-KASIL #6

Fig. 10 FIBROUS SPECIMENS IMPREGNATED WITH NONMETALLIC FILLERS evaporation to 50 per cent solids.

Slurry No. 1

talc, 47 per cent by wt.
potassium silicate, 25 per cent
diluting water, 28 per cent

Slurry No. 2

talc, 45 per cent by wt.
silicone, 55 per cent

Slurry No. 3

cadmium sulfide, 35 per cent by wt.
talc, 23 per cent
potassium silicate, 12 per cent
diluting water, 30 per cent

Slurry No. 4

cadmium sulfide, 5 per cent
silver, 50 per cent, talc 5 per cent
potassium silicate, 10 per cent
diluting water, 30 per cent

Slurry No. 5

talc, 70 per cent
3 M material, 30 per cent

Slurry No. 6

talc, 10 per cent
copper, 67 per cent
potassium silicate, 7 per cent
diluting water, 16 per cent

In the foregoing preparations, the source of potassium silicate is Kasil No. 6, a liquid preparation containing 40 per cent solids, supplied by Philadelphia Quartz Company. The silicone is the SR-32 described previously. All solid components of the slurries were less than 325 mesh particle size.

Samples of 430 stainless steel bonded skeleton of 23 per cent density were used for impregnation. Discs of 2-inch diameter and 1/8-inch thickness were impregnated for evaluation as gaskets in a pressurized flange. Cylinders of 1/4-inch diameter and 3/8-inch length were impregnated for evaluation of friction.

The skeleton samples were mounted with appropriate rubber supports in a funnel so that a slurry could be drawn through them. A reservoir of slurry was maintained over the sample as suction was applied. After adequate flow was established, suction was discontinued. The sample was taken from the funnel, wiped to remove excess material, then oven dried and baked finally to at least 250°C.

It was necessary to repeat the impregnation and baking four or five times. At first, gentle suction was sufficient to draw slurry into the skeleton. As the treatments progressed, increasingly greater suction was needed. Finally, very little material could be drawn in with a vacuum near 30 inches of mercury. Complete filling of the skeleton samples was difficult to obtain. The solid components of the slurries filtered out and packed on the surfaces before interior voids could be adequately filled.

D. Friction and Wear Studies

The procedure and apparatus used to evaluate friction and wear is as described in a prior section of this report. The performance of the fiber metal composites with nonmetallic impregnants is shown in Table 6.

Wear and damage was very noticeable with skeletons filled with talc-silicone slurry. Such samples disintegrate on contact with a moving surface, and their breakdown is accelerated with heating. An addition of powdered silver to an impregnant containing cadmium sulfide, talc, and potassium silicate appeared to aid lubrication and minimize plate scoring. Skeletons filled with the slurry supplied by Minnesota Mining were structurally weak.

E. Static Seal Evaluation

To evaluate static sealing ability, impregnated skeleton samples, 2-inch diameter by 1/8-inch thickness , were used as gaskets in a special flange assembly shown in the Part I report (page 85). Each gasket was compressed in the flange with six mounting bolts. A source of pressurized air was connected to the flange. Leakage through the gasket body and around its compressed edge was determined separately by connections to allow bubbling of the escaping air through a water reservoir. For evaluation at 1200°F, the flange assembly was enclosed in an electric furnace.

The usual procedure was to secure the skeleton sample in the flange with a low bolt torque of 5 ft-lb. Air under controlled pressure was admitted, and the pressure at which leakage started was recorded. Usually leakage occurred first through the gasket body rather than around its compressed edge. The tube to detect this leakage was then plugged. Next, torque on the flange bolts was increased by stepwise increments, and pressures at which leakage occurs around the edge of the gasket were recorded. An objective was to obtain a seal for 5000 psi air pressure. In attempts to reach this maximum pressure, a torque not exceeding 100 ft-lb was used on the flange bolts.

After the gasket was compressed to its final operating pressure, the flange assembly was heated to 1200°F. Pressure retained at the elevated temperature was determined. The assembly was cooled, and the torque on the flange bolts was checked. Usually the bolts were loose after heating. The bolts were therefore tightened to their original setting, and the assembly was reheated and evaluated for leakage at 1200°F. The heating and cooling cycle was repeated at least three times.

Reproducible results were difficult to obtain with the ceramic filled skeletons. The samples were not easily compressed and tension on the bolts changed constantly. Results varied widely among samples of the same composition. Erratic performance was due apparently to incomplete impregnation of the skeletons and to their poor compressibility and resiliency.

Table 6

FRICTION AND WEAR CHARACTERISTICS OF IMPREGNATED FIBER METAL SEALANTS

Composition	Sealant Weight Loss, per cent	Sealant Wear Rate, in./min	Break-away Friction, lb	Remarks
430 SS, bonded, 23 per cent skeleton density, impregnated with talc-silicone slurry				Evaluated at room temperature, 500°F and 1200°F. At all temperatures, sealant grinds to powder. Some scoring of plate also.
430 SS, bonded, 23 per cent skeleton density, impregnated with talc-potassium silicate slurry	0.88	0.002	5	Plate scored.
430 SS, bonded, 23 per cent skeleton density, impregnated with cadmium sulfide-talc-potassium silicate slurry	1.9	0.0008	4	Sealant develops polished appearance. Some scoring of plate.
430 SS, bonded, 23 per cent skeleton density, impregnated with cadmium sulfide-talc-silver-potassium silicate slurry	0.25	0.0008	4	Smooth operation; very light scoring of plate.
430 SS, bonded, 23 per cent skeleton density, impregnated with copper-talc-potassium silicate slurry	1.2	0.001	5	Plate deeply scored.
430 SS, bonded, 23 per cent skeleton density, impregnated with fibrous slurry from Minnesota Mining	15.3	0.019	4	Sealant flattened and wore rapidly; plate badly scored.
430 SS, bonded, 23 per cent skeleton density, impregnated with mixture of talc and fibrous slurry from Minnesota Mining.	2.7	0.003	6	A few deep scores in plate.

Test Conditions: 1200°F
Rubbing Speed: 55 ft/min
Load on Sealant: 4 lb (80 psi)
Running Time: 5 min

In Table 7 are listed measurements for the best samples of each composition. For comparison with the impregnated samples, a non-impregnated skeleton covered on the top and bottom with a sheet of 0.005-inch thick silver foil, was included in the investigation.

All of the impregnated samples were permeable to low pressure air. Leakage through the body was evident in the range from 5 to 15 psi air pressure. Only the sample covered with silver foil provided a non-permeable body. It remained leak free until the foil was punctured by compressive forces in the test flange. The values tabulated in Table 7 represent pressure at each torque setting at which leakage occurs around the compressed edge of the impregnated gaskets.

In general, very little sealing ability was demonstrated until the impregnated skeletons were compressed with relatively high torque forces on the flange bolts. Exceptions were the skeleton filled with talc-silicone and the non-impregnated skeleton covered with silver foil. Initially these two gaskets were well secured with a moderate torque of 35 ft-lb. On heating, decomposition occurred in the silicone gasket so that eventually 100 ft-lb was required to maintain a seal at 5000 psi pressure. With the silver covered skeleton, an operating pressure over 2000 psi could not be obtained. The silver punctured when a torque greater than 35 ft-lb was applied to the flange bolts.

As shown in Table 7, only the sample impregnated with talc-silicone slurry was capable of retaining 5000 psi air pressure at room temperature and at 1200°F. After once heating to 1200°F and re-tightening the bolts, leak free sealing to 5000 psi was obtained with repeated heating and cooling. It was found by visual examination that this type of gasket was more completely filled with impregnant than any of the other compositions tested. This may account for its superior sealing ability.

Impregnation with talc-potassium silicate provided a gasket which initially appeared to seal poorly. After heating, the gasket was more easily compressed, and pressure up to 4500 psi was retained. Good seal performance persisted with subsequent temperature cycling.

Less erratic results were noted with a skeleton impregnated with a mixture of cadmium sulfide, talc, and potassium silicate. At a low bolt torque, it showed measurable sealing ability which increased in substantial increments as greater torques were applied. A final pressure of 3500 psi was retained with a torque of 100 ft-lb. No change was detected on aging at 1200°F or in repeated cycling to 1200°F. Poor performance was observed with the other compositions listed in Table 7. Their inability to seal may be due to the impregnant composition. However, it is suspected that these skeletons were not adequately filled.

Table 7

PERFORMANCE OF IMPREGNATED FIBER SKELETONS AS GASKETS IN STATIC FLANGE

Compositions	Talc-potassium silicate impreg.	Talc-silicone impreg.[1]	Cadmium sulfide talc-potassium silicate impreg.	Cadmium sulfide talc-silver-potassium silicate impreg.	Copper-talc-potassium silicate impreg.	Minn. Mining Slurry impreg.	Minn. Mining with talc for impreg.	Skeleton covered with silver foil[2]
	Pressure at which Leakage Starts, psi, around the Compressed Edge of Gasket							
Torque on flange Bolts ft-lb								
5	15	10	65	10	10	5	5	120
15	20	220	110	10	10	5	10	275
25	20	3400	250	10	10	5	25	440
35	20	5000	500	15	10	5	50	2000
50	30		1500	15	10	5	80	
70	75		2500	80	90	15	180	
100	510		3500	195	135	40	240	
	Pressure retained at 1200°F							
100	4500	5000	3500	195	150	45	1000	1400 with 40 ft-lb torque

---

[1] Silicone stuck to flanges, necessitating re-machining of flanges.

[2] No leakage through gasket body until foil was pierced when over 35 ft-lb torque and 2000 psi air pressure were applied.

V. NON-FIBROUS COMPOSITES

A. Ceramics

The refractory materials are desirable for applications where heat resistance property is needed. Various experiments have been conducted with these materials in order to utilize them in composite combinations for use as seals. Information obtained from these experiments indicated that specimens produced by the generally accepted methods were too porous. The main problem seems to be the lack of suitable binders. Commercially obtainable binders and fillers that were used in our experimental work are given below.

Binders	Fillers
Colloidal silica	Talc
Mono-aluminum phosphate	Natural and synthetic mica
Liquid sodium and potassium silicates	Clay
Glass	Boron nitride
Metal powders	Asbestos
Teflon	Silica Fiber
	Chromium oxide Cr_2O_3

Experiments were performed to obtain some indication of the performance of the ceramic composite materials in contact with a movable metallic surface at 1200°F, and the results are presented in Appendix II.

1. Talc Composites

To determine whether non-metallic substances such as ceramics could be utilized by themselves to form seals, a number of experiments of a preliminary nature were performed.

Relatively dry mixtures were prepared with enough binder to permit fabrication of bodies by pressure molding. Using a steel, plunger-type die, each mixture was pressed into discs of 1-7/8-inches and 1/8-inch thickness. A pressure of 10,000 psi was found adequate for good compaction. The discs were inspected visually for mechanical strength and possible damage on exposure to 1200°F. Their apparent porosity before and after heating were evaluated with compressed air in the test fixture designed to detect flow through the sealant body. Compositions which were studied and their performance are summarized in Table 8.

Nearly all of the bodies were much too porous to prevent the flow of pressurized air. Leakage was evident at 10 psi, quite rapid at 90 psi, and occurred through the sealant rather than around its gently compressed edges. Non-porous bodies were obtained with either teflon dispersion or with glass. Teflon bonded talc, however, becomes porous with heating and progressively deteriorates with continued exposure to temperature above 500°F. Talc bonded with a lead borosilicate frit (PB461),

Table 8

CHARACTERISTICS OF TALC BODIES BONDED WITH VARIOUS BINDERS

Mixture	Remarks
50 grams Talc 15 c.c. Nalcoag (Colloidal Silica Dispersion)	Easily pressed into discs. A relatively soft or weakly bonded body. Very porous before and after heating to 1200°F.
50 grams Talc 15 c.c. Kasil No. 6 (Potassium Silicate Liquid)	Pressed discs air-harden to form strong material. Binder does not blister on heating. Body remains stable at 1200°F. It is porous to 40 lbs. air pressure.
50 grams Talc 30 c.c. Teflon 30 Dispersion	Rather soft, easily compressed discs. Body not porous until heated to expel water. The dried material can be re-pressed to form impervious disc. Leakage again starts at 500°F with noticeable odor of Teflon decomposition. Discs exposed to 500°F can be compacted further to temporarily stop leakage. At 650°F, noticeable weakening occurs whereas at 750°F the discs rapidly disintegrate.
50 grams Talc 40 grams Teflon Powder	Not as non-porous or as heat resistant as the discs formed with the Teflon dispersion. Powdered resin was difficult to distribute uniformly through the talc.
50 grams Talc 10 c. c. Mono-aluminum phosphate liquor	Strong body, thermally stable at 1200°F. Porous to 40 lbs. of air pressure.
25 grams Talc 75 grams glass Frit PB461 20 c.c. Nalcoag	Fired to 1350°F to produce a vitreous bond. Very brittle discs subject to cracking on rapid heating and cooling. Discs usually broke when porosity evaluation was attempted. Tests indicated that the composition should contain more glass to insure total sealing of the pores.
10 grams Talc 90 grams Powdered Silver	Discs rather difficult to fabricate. Material binds in the die. A rather weak body but noticeably strengthened after heating to 1200°F. Porous to low pressure air.

after curing at a fusion temperature of 1350°F, provides a vitreous, impervious body. These discs are brittle and break easily if not properly positioned in the test flanges. Reliable evaluation of porosity was difficult to obtain.

Relatively soft, easily crushed bodies are obtained with a Nalcoag binder. Talc-teflon compositions are compressible but are easily torn apart. Silver-talc mixtures appear to have some compressibility and toughness. Strong bodies result with potassium silicate and aluminum phosphate bonding. The strongest discs were those of glass bonded talc. These also are the most brittle.

The foregoing experiments were repeated using a hot die to form discs rather than room temperature pressing. This procedure was used with the aqueous binders, Nalcoag, potassium silicate, mono-aluminum phosphate, and Teflon 30. An objective was to expel volatile water as the disc is being formed. Thus, more dense, less porous bodies were expected.

The die was pre-heated to 800°F. It was then transferred to the press and filled with an appropriate quantity of each mixture. A pressure of 10,000 psi was applied and maintained for 15 minutes while the formed disc baked in the die.

Talc-potassium silicate discs appeared to be better bonded by hot pressing and to be nearly impervious to 90 psi air. However, leakage was detected after the samples aged in a furnace at 1200°F. Nalcoag, aluminum phosphate, and Teflon 30 binders appeared to dehydrate before good bonding with the talc would be established. Weak, porous structures were obtained.

2. Glass Composites

Additional discs were made with mixtures containing the lead borosilicate frit. Boron nitride, natural mica, and blue asbestos (Grade H, North American Asbestos Corporation) were used as fillers. The objective was to produce non-porous bodies by bonding a relatively large volume of these light weight materials with a small volume of the heavy glass. Weight compositions used to produce the mixtures are listed in Table 9.

All preparations were fired to 1350°F, a temperature sufficient to vitrify the glass. Best results were obtained with the boron nitride composition. These discs are non-porous to 90 psi air and are resistant to cracking. Mica compositions persisted in bloating on firing. Glass bonded asbestos contained many voids, and cracked apart on cooling. No improvement was obtained by using pre-fired mica and asbestos in the formulations. Asbestos fibers were found also to crumble after 1200°F heating.

Table 9

GLASS BONDED COMPOSITIONS

Fused at 1350°F

Mixture	Remarks
10 grams Boron Nitride 90 grams Frit PB461 Pemco Company 13 c.c. Nalcoag	Well bonded body. Resistant to cracking on heating and cooling. Non-porous to 90 psi air.
10 grams Blue Asbestos 50 grams Frit PB461 15 c.c. Nalcoag	Well fused body but cracks on cooling. Contains voids.
20 grams Natural Mica 50 grams Frit PB461 15 c.c. Nalcoag	Bloats on firing. Very poor structure.

Porous bodies were, of course, expected with the simple talc preparations containing the various liquid binders. It was hoped that they would not be as porous as was indicated by their leakage of low pressure air. Powdered metal such as pliable silver was found to serve as an effective binder for talc and to provide a body with slight compressibility. It may be possible to obtain impervious bonding by heating the bodies to partially fuse the silver. The merits of colloidal silica (Nalcoag), potassium silicate, mono-aluminum phosphate, Teflon 30, and powdered metal binders may be more evident as friction and wear characteristics are determined. Compositions useful with solid backing materials may result.

B. Friction and Wear Studies

The apparatus used to obtain friction and wear data for non-fibrous composites is described in a previous section and in Appendix I of this report.

Materials which exhibited favorable characteristics under less stringent conditions were evaluated at higher velocities and pressures.

The arrangement and components of the apparatus used in these experiments are described and illustrated in Appendix I.

Samples were prepared by mixing various available ceramic materials with binders like Nalcoag, potassium and sodium silicates, teflon, mono-aluminum phosphate, glass, and precipitated silver powder.

Ceramic powders (325 mesh) were combined by milling with enough binder to form mixtures for cold pressing. A pressure of 100,000 psi provided dense, well compacted samples. Each fabricated composition was oven dried, then heated slowly, and fired at a final temperature of 1200°F for two to three hours. After firing, the circular faces of the samples were inspected, and if required, ground flat before insertion in the experimental assembly.

The material combinations which were prepared and subjected to the observations and friction studies can be separated into two groups:

1. Specimens made of talc with various refractory binders
2. Materials representing the usual refractory oxides, fluorides, sulfides, silicates, and platey materials like boron nitride, mica, clay, graphite, and molybdenum disulfide.

2. Experimental Results

Experimental data are tabulated and presented in Appendix II. Tables 13, 14, and 15 are self-explanatory. However, some additional explanatory remarks on each group are in order and will be given below.

a. Six compositions, which were subjected to friction and wear studies, are listed in Table 13. Comparative rather than absolute data are presented.

Samples prepared with Nalcoag were too weak to withstand the experimental conditions. Teflon bonded material was found to disrupt and disintegrate rapidly at temperatures of 750°F and above. At 450°F, this material was subject to plastic deformation and was not sufficiently durable for testing. The aluminum phosphate composition is quite hard but wears rapidly and scores the plate deeply. Slight melting was observed in the glass composition indicating that perhaps more refractory glass should be used. The Pemco glass No. 461 rapidly fuses at 1400°F, but apparently softens or sinters at somewhat lower temperatures. Sodium and potassium silicates provide bodies of about equal performance. However, bodies fabricated with the potassium compound were found less likely to blister on curing and to contain fewer laminations. The best results were obtained with a simple mixture of talc and silver powder. Under pressure, the highly workable silver flows and provides an effective binder for the talc.

Sample No. 6 represents an optimum composition of the silver-talc combination. An increase in talc results in a lower lubrication effect, whereas an increase in silver provides a body subject to deformation.

Thus, it appears, on the basis of wear measurements and general observations, that continued preparation of ceramic composites for evaluation should be made with binders such as potassium silicate, glass, and silver. Since results were particularly outstanding with silver, other metal powders were immediately included in the investigation.

b. Table 14 lists a number of preparations representing the usual refractory oxides, fluorides, sulfides, silicates, and the platey boron nitride, mica, and clay. Thermally unstable graphite and molybdenum disulfide were used in conjunction with glass to restrict their oxidation with a protective glass layer. The wear properties of "Solution Ceramic" coatings, deposited by a thermal spray process, were evaluated. Special DuPont products such as fibrous potassium titanate and phthalocyanine, a heat resistant organic compound, were included in the study. Metal powders of chromium, nickel, aluminum, copper, and iron were investigated.

Most of the compositions listed in Table 14 were found to either wear rapidly or to abraid the mating plate badly. Favorable results were obtained only when the interface between the body and plate was polished to a glossy surface. Many of the preparations contain talc. This material aids the fabrication of bodies and appears to contribute to low wear performance.

Composites bonded with silver, or silver in combination with potassium silicate or Nalcoag binders, again demonstrated the desirable lubricating effects of this metal. Attempts to substitute other powdered metals resulted in mixtures more difficult to fabricate and provided bodies of poor performance. Exceptions were copper and nickel, but these materials were definitely inferior to the more pliable silver. In addition to silver, other composite ingredients which appear to be desirable are cadmium sulfide, lead sulfide, and possibly mica.

c. Additional data are tabulated in Table 15 for those compositions which were found during previous experiments to exhibit low wear rates and to be least damaging to the moving metal plate. As indicated in the table, two sets of conditions were used. First, the pressure of 80 psi against the plate was maintained as during the previous experiments, but the running time was extended to 15 minutes and the rubbing velocity was increased from 55 to 65 ft/min.

The second condition was similar to the first except that the pressure against the plate was increased from 80 to 160 psi.

The slightly higher surface velocity and longer running period resulted in no significant change in the performance of the selected compositions. All continued to exhibit low wear, some lubrication, and particularly, the beneficial effects of silver. Evaluation under a 160 psi specimen loading, however, produced definite changes. The simple talc-silver composite (No. 6) deformed under the increased pressure. Talc-copper (No. 26) was decidedly abrasive. Scoring and sample wear was evident with cadmium sulfide (No. 38). Lead sulfide (No. 51) was damaging to the mating plate. The best composition is represented by No. 48. This is basically a talc-silver combination, but is reinforced with potassium silicate for mechanical strength and modified with cadmium sulfide for lubrication.

VI. SEALING STUDIES

A. Low Pressure Seals

As discussed in the section on metallic coatings, a low pressure seal (15 psi) which will withstand 1200°F would be useful as a gasket for space vehicles and other purposes. Some disadvantages were listed which indicate that other approaches to this problem should also be considered. Therefore, it was decided to test other candidates, which were available in the form of 0-rings.

1. Test Apparatus

The principal part of the test apparatus is a fixture shown schematically in Fig. 11.

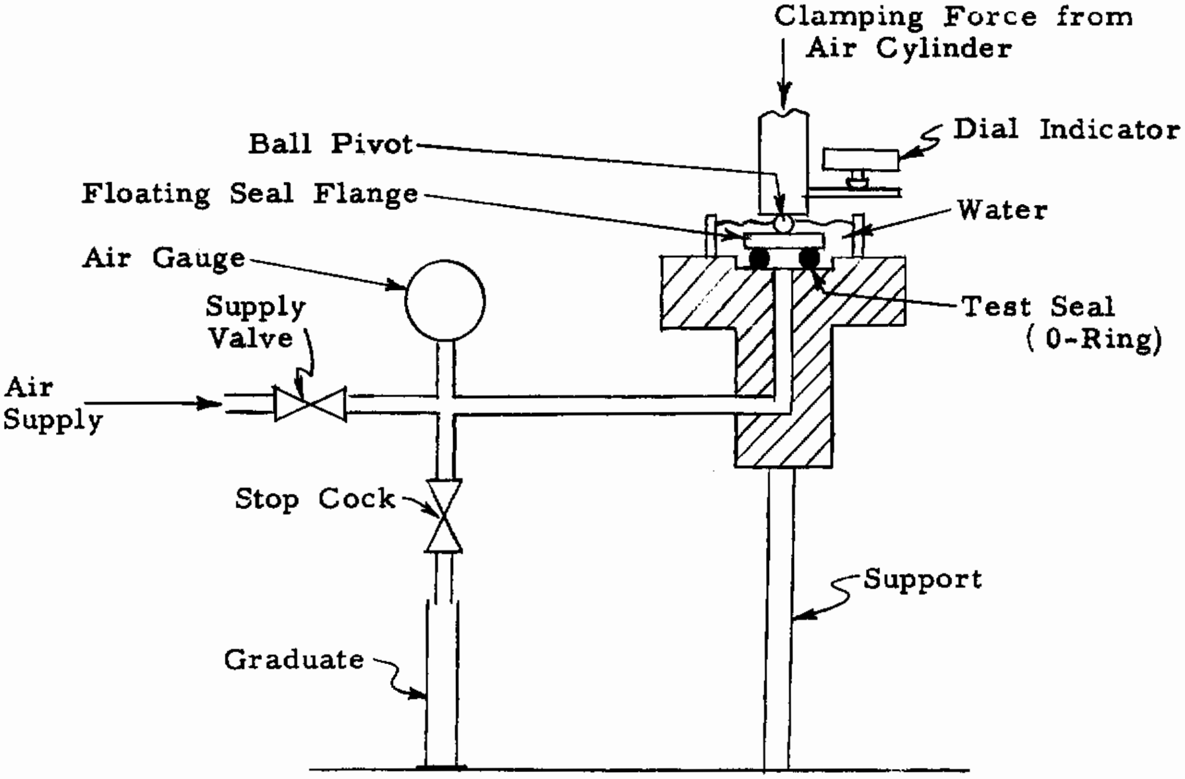


Fig. 11 SCHEMATIC OF LOW PRESSURE TEST FIXTURE

To ensure that the pressure was evenly distributed all around the 0-ring, a hardened steel ball was introduced between the air cylinder plunger and the floating seal flange. The seal was immersed in a water bath, and provision was made for introducing air pressure into the 0-ring seal. A dial indicator is used to measure the amount of compression of the seal. A photo of the fixture is shown in Fig. 12.

The complete apparatus is shown in Fig. 13, where the pressure regulator for controlling the compressed air pressure to the air cylinder is shown to the left of the fixture.

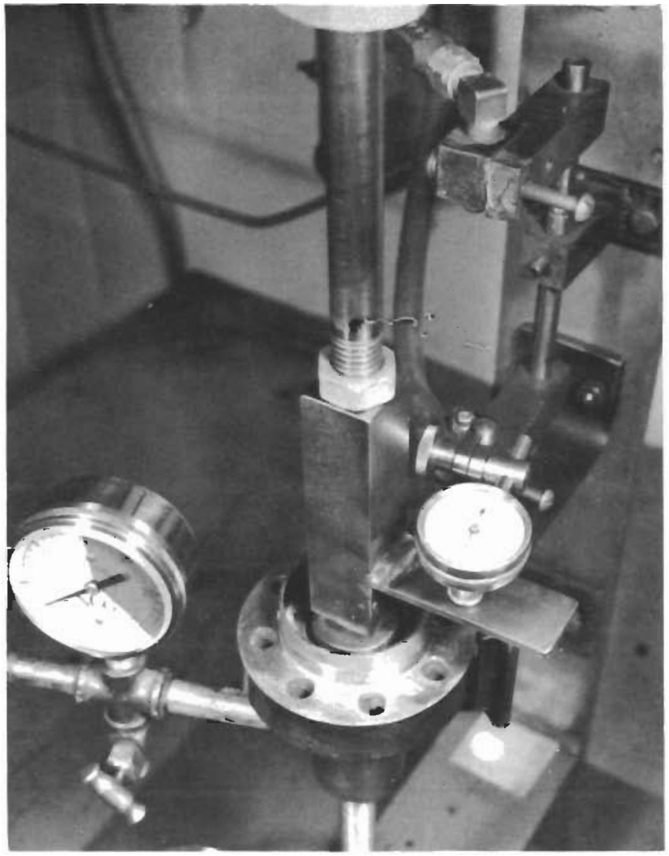


Fig. 12 FIXTURE FOR TESTING LOW PRESSURE O-RING SEALS

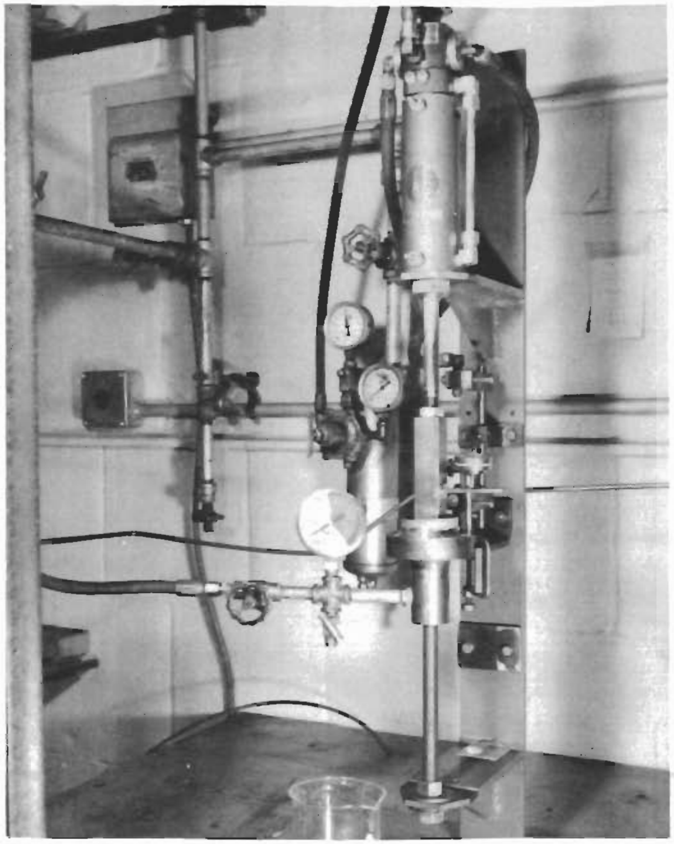


Fig. 13 COMPLETE APPARATUS FOR TESTING LOW PRESSURE O-RING SEALS

2. Test Procedure

To perform a test, the seal is installed in the fixture as shown in Fig. 11. A small clamping force is placed on the seal by the air cylinder and water is poured around the seal. If the water leaks through the seal, it trickles down through the hole in the fixture and out through the pipe and stop cock, where it falls into a beaker. The clamping force is increased until the point is reached when no water leaks through the seal, or when the maximum clamping force of the cylinder (about 250 lbs.) is reached.

At this point air is introduced into the 0-ring seal. At some small pressure, usually 2 psi, the supply valve is shut and leakage is detected by watching the air gauge and by noting bubbling through the water. If there is no leakage, the air pressure is gradually raised until leakage is detectable, or until 25 psi is reached, which is well above the desideratum of 15 psi.

3. Test Results

The sample materials tested are listed below. In each case the 0-ring size was 1/4-inch I.D. x 5/8-inch O.D. x 3/16-inch thick and a skeleton of 430 stainless steel fibers, bonded, with a 23 per cent skeleton density, was used unless otherwise noted.

No. 1	Impregnated with cadmium sulfide, talc, silver, potassium silicate
No. 2	Impregnated with talc, silicone
No. 3	Impregnated with talc, potassium silicate
No. 4	Impregnated with cadmium sulfide, talc, and potassium silicate
No. 5	Same as No. 4, except seal surface was re-faced by hand lapping
No. 6	Impregnated with phosphonitrillic chloride (organic rubber) and immersed in a solution of KNH_2 in liquid ammonia. Hand lapped.
No. 7	Impregnated with a partially cyanolated phosphonitrillic chloride and immersed in a solution of KNH_2 in liquid ammonia. Hand lapped to remove high spots.
No. 8	Bare skeleton, hand lapped.
No. 9	Crystal M (synthetic mica) with ceramic fiber K filler 1/4-inch I.D. x 5/8-inch O.D. x 3/32-inch thick

No. 10 Same as No. 9

No. 11 Same as No. 9

Table 10 summarizes the results of the tests. The most promising material of the group appears to be Crystal M[1], Nos. 9, 10, and 11. A clamping force of about 31 lbs. was necessary to seal against 15 psi air pressure. Since the 0-ring has a mean circumference of about 1-3/8 inches, the clamping force per lineal inch is about 22.5 lbs. This compares with a clamping force required for most elastomeric seals of about 5 to 10 lbs. per lineal inch. The advantage of the Crystal M material is its much greater temperature resistance (about 1800°F). It is felt that the performance of some of the other materials tested will be improved if the problem of impregnation is overcome.

The bare skeleton ring, No. 8, was tested to estimate its value as the structural element of a low pressure seal. The data indicates that the clamping force required for the same compression is about the same as for the Crystal M. However, the addition of fillers for sealing may raise the clamping force. Investigation of fibers of other sizes, configurations, and materials should be carried out to reduce the clamping force.

Figure 14 shows some of the seals used in the evaluation.

B. Reciprocating Shaft Seals

As reported in an earlier section of this report, Armour Research Foundation material showed promise when used as reciprocating shaft seals by Republic Aviation at 4000 psi and 1000°F. It was therefore decided to explore this application with the objective of finding the simplest design of seal, packing gland, and stuffing box which will give desirable results.

1. Test Apparatus

The principal part of the apparatus is the fixture shown in cross-section in Fig. 15.

A photograph of the fixture is shown in Fig. 16. The two halves of an electric furnace are shown in open position. The complete apparatus is pictured in Fig. 17, which shows the fixture enclosed by the furnace. A reciprocating cylinder is located above the fixture and is connected to it with a universal joint. The hose at the right of the picture feeds temperature resistant hydraulic fluid to the fixture, and is connected to an accumulator (not shown) actuated by high pressure air. The temperature resistant fluid designated MLO-59-692, is structurally a bis (phenoxy phenoxy) benzine which will withstand 1000°F for short periods of time and 800°F indefinitely.

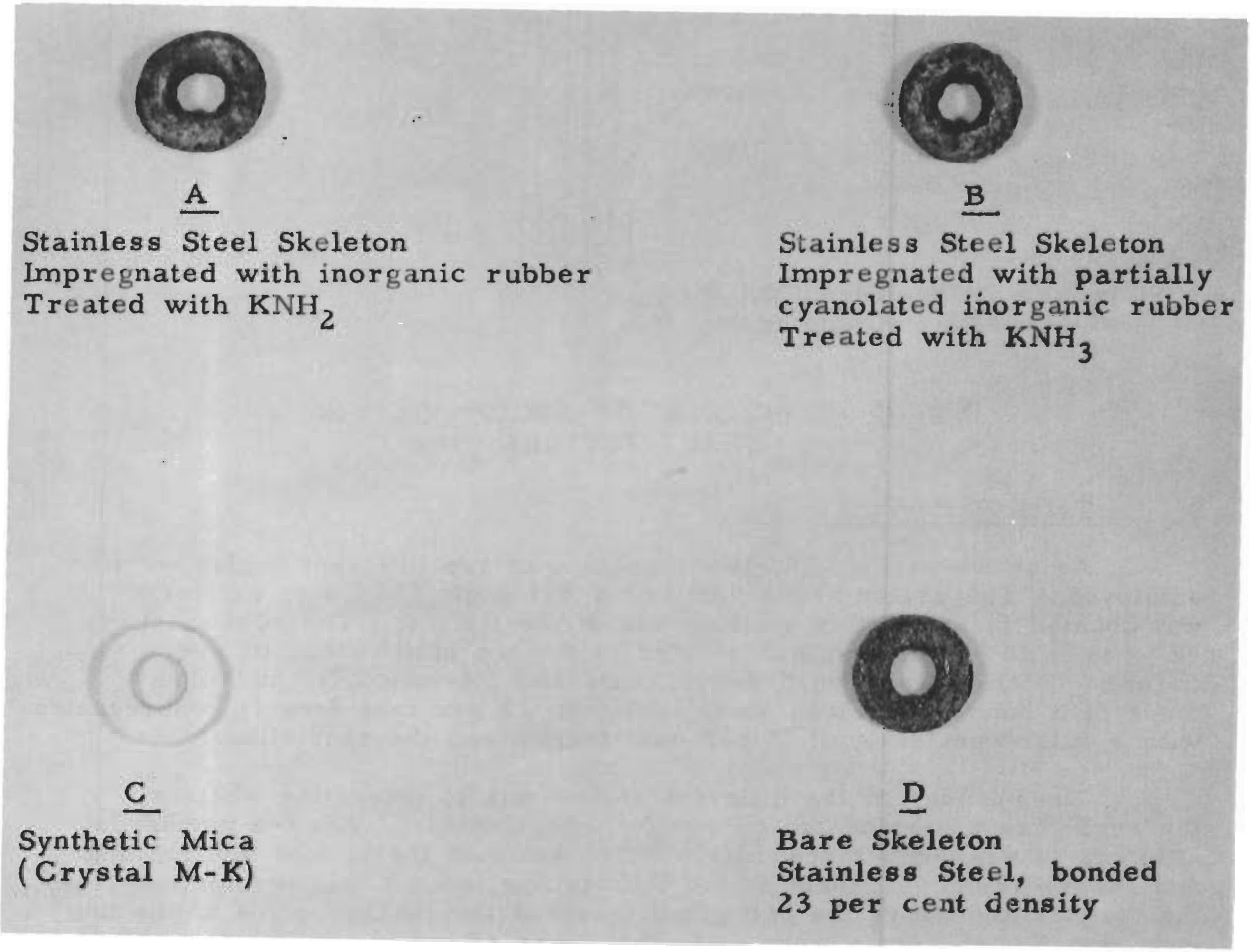
---

[1] Made by Minnesota Mining and Manufacturing Company, St. Paul, Minn.

Table 10

LOW PRESSURE SEAL EVALUATION

Sample No.	Clamping Force, lb.	Compression, in.	Air Pressure on Seal, psi	Leakage	
				Water drops/15 sec.	Air
1	250	.0105	2	1	Profuse
2	250	.0115	2	3	Profuse
3	250	.011	2	0	Profuse
4	250	.0075	2	3	Profuse
5	250	.001	2	0	Slowly
6	250	.0045	2	0	Slowly
7	250	.0032	2	0	Slowly
8	250	.054	-	-	
9	94	.022	25	0	0
10	16	.016	10	0	Slowly
11	31	----	15	0	0



A

Stainless Steel Skeleton
Impregnated with inorganic rubber
Treated with KNH_2

B

Stainless Steel Skeleton
Impregnated with partially cyanolated inorganic rubber
Treated with KNH_3

C

Synthetic Mica
(Crystal M-K)

D

Bare Skeleton
Stainless Steel, bonded
23 per cent density

Fig. 14 TYPICAL SEALS USED FOR LOW PRESSURE SEAL EVALUATION

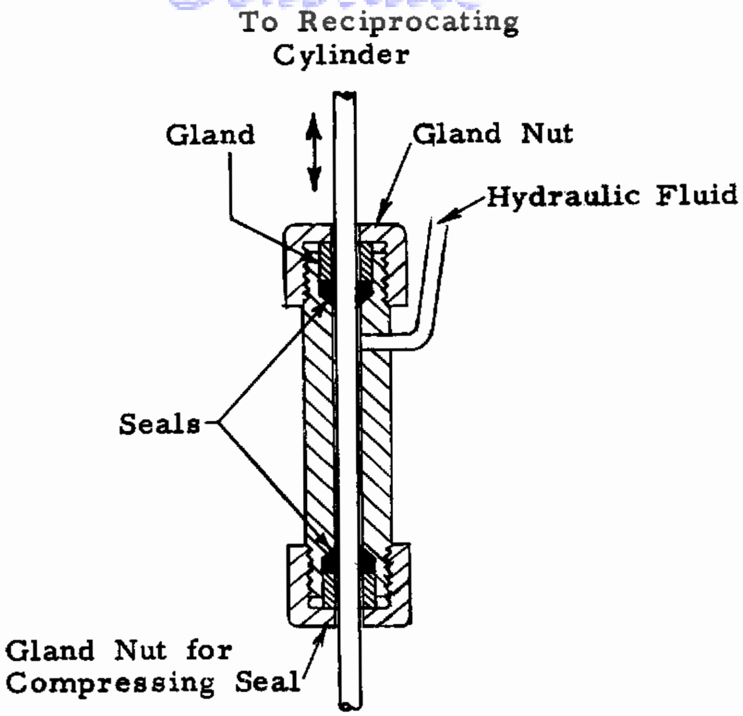


Fig. 15 SCHEMATIC OF RECIPROCATING SHAFT FIXTURE

2. Tests Performed

As shown in Fig. 18, bevel seals with two different angles were employed. The seal marked "A" has a 30° angle (60° with axis) and was located in the bottom stuffing box of the fixture. The seal marked "B" has a 45° angle and was located in the top stuffing box of the fixture. Both seals were 5/8-inch O.D. and 1/4-inch I.D. and were made of a bonded stainless steel skeleton, 23 per cent density, impregnated with a filler consisting of 16 per cent indium and the rest silver.

The purpose of the different angles was to determine whether the angle has a bearing on the sealing effectiveness. After a number of attempts to seal with three different 30° seals at the bottom stuffing box and two different 45° seals at the top stuffing box, it was determined from the torques applied to the two gland nuts and the leakage rates at the two ends that the 45° seals were somewhat more effective.

Also shown in Fig. 18 are two shafts. Shaft "C" was made of No. 303 stainless steel with a hardness of 23 Rockwell C. Shaft "D" was made of No. 440c stainless steel, hardened and ground, with a hardness of 56 Rockwell C. Both shafts are 1/4-inch diameter and 13 inches long.

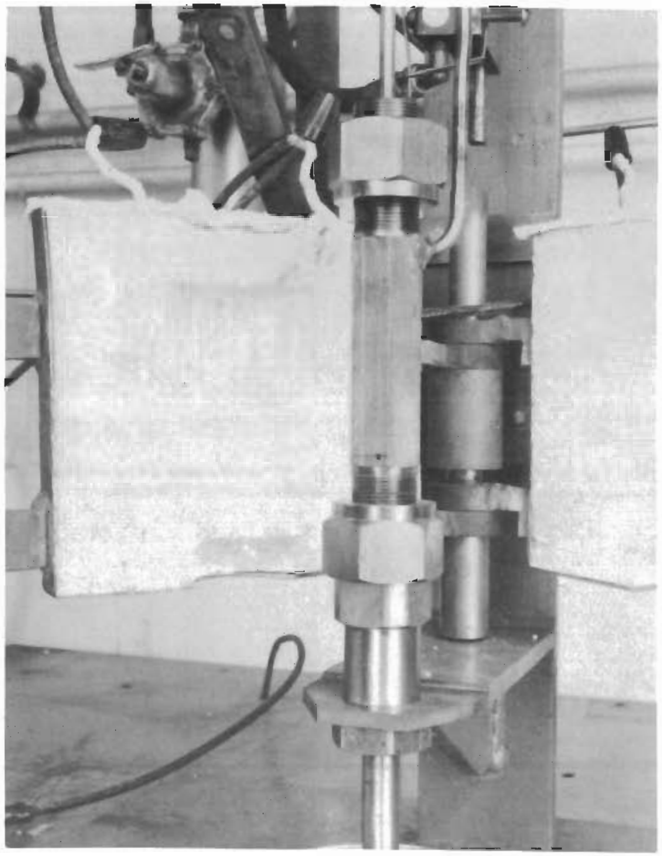


Fig. 16 FIXTURE FOR TESTING RECIPROCATING SHAFT SEALS

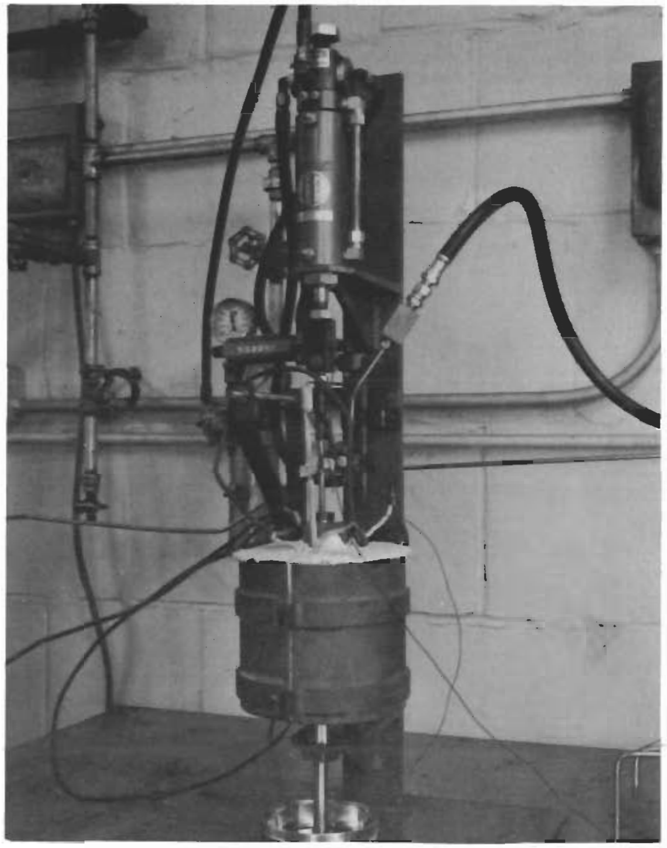


Fig. 17 COMPLETE APPARATUS FOR TESTING RECIPROCATING SHAFT SEALS

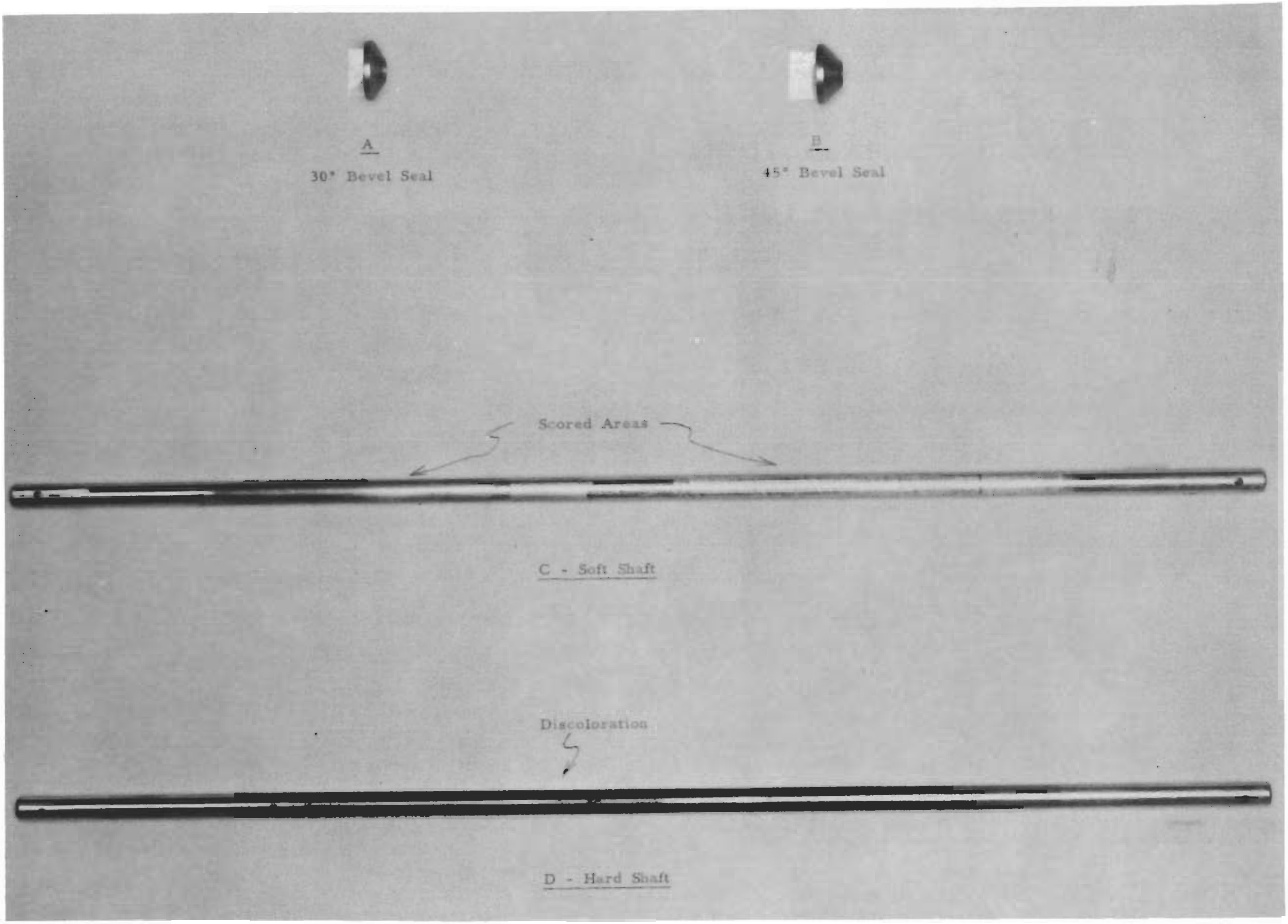


Fig. 18 SEALS AND SHAFTS FOR RECIPROCATING FIXTURE

The purpose here was to determine the type of shaft material necessary for effective sealing. As expected with the softer shaft, the fiber ends in the seals scored the shaft. The harder shaft was not affected by the fibers. The discoloration shown came from varnish deposits from the hydraulic fluid when operating above 800°F.

Since leakage was still encountered with 45° seals at both ends and with the harder shaft, further changes should be made to the fixture, such as the following:

1. The lower end of the fixture should be closed off and the shaft should be shortened so it is necessary to seal at only the top end. This would probably involve changing the cylinder also, since there will be an additional load from the hydraulic pressure on the rod end.
2. Belleville washers should be tried to see if they are more effective in taking up wear than the resilience of the seal itself.
3. The finish on the seals should be improved. Presently the bores are honed and the beveled portions are lapped with the seats. However, the metal fibers are considerably harder than the fillers, so the surfaces are sometimes uneven when seen under a microscope.
4. The length of the seals should be reduced to determine whether this will make sealing more effective or if less torque is required.
5. Shaft coatings, such as hard chrome, should be tried to see whether this improves sealing.

C. Rotating Shaft Seals

Since no outside organization has applied the Armour Research seal material to rotating shaft seals, it was decided that some of the parameters necessary for this type of seal should be investigated. The objective was again to find the simplest design of seal and stuffing box which will give desirable results.

1. Test Apparatus

The heart of the apparatus is the fixture shown in cross-section in Fig. 19.

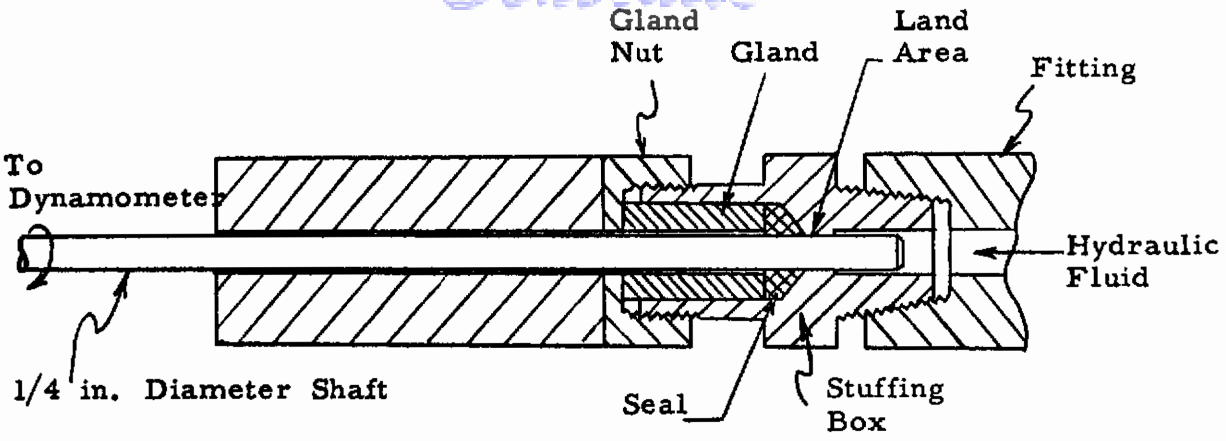


Fig. 19 CROSS-SECTION OF ROTATING SHAFT FIXTURE

The fixture is also shown in Fig. 20. An electric furnace is shown in open position. To the left is a beaker for catching leakage, and to the right is the ice container used for the cold junction of the thermocouple. Hydraulic fluid enters the fixture through the tubing at the right of the fixture. Figure 21 pictures the complete set-up, which employs a three horsepower dynamometer, shown with its scale and controls to the left of the fixture. The dynamometer is connected to the rotating shaft by means of a universal joint. The fixture and furnace (shown closed) are enclosed by clear plastic sheets on all sides and a hood on top as a safety precaution during heating of the hydraulic fluid.

2. Tests Performed

Figure 22 shows some of the seals used in the rotating shaft stuffing box. The seal marked "A" has a 30° angle (60° with axis) and was the first type tried. The seal marked "B" shows the result of excessive clearance between the shaft and parts adjacent to the seal. Both the gland and stuffing box had a bore about 0.010 in. greater than the shaft diameter, allowing extrusion on both sides of the seal as shown. For this reason, a new gland was made with about 0.002 in. clearance and a new stuffing box was made with a land area having about 0.001 in. clearance. The new stuffing box had a 45° seat, as this was considered to be better for sealing than a 30° seat.

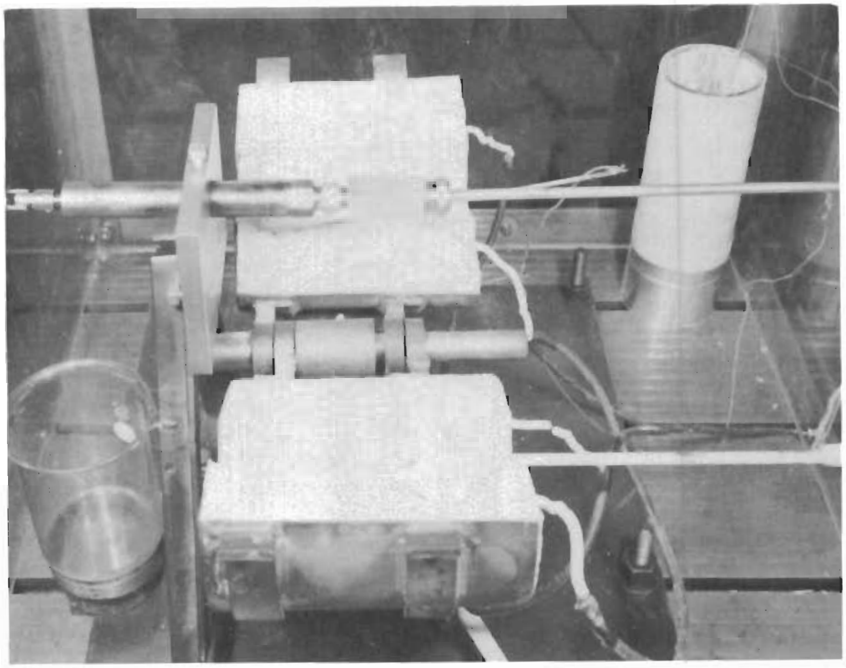


Fig. 20 FIXTURE FOR TESTING ROTATING SHAFT SEALS

Fig. 21 COMPLETE APPARATUS FOR TESTING ROTATING SHAFT SEALS

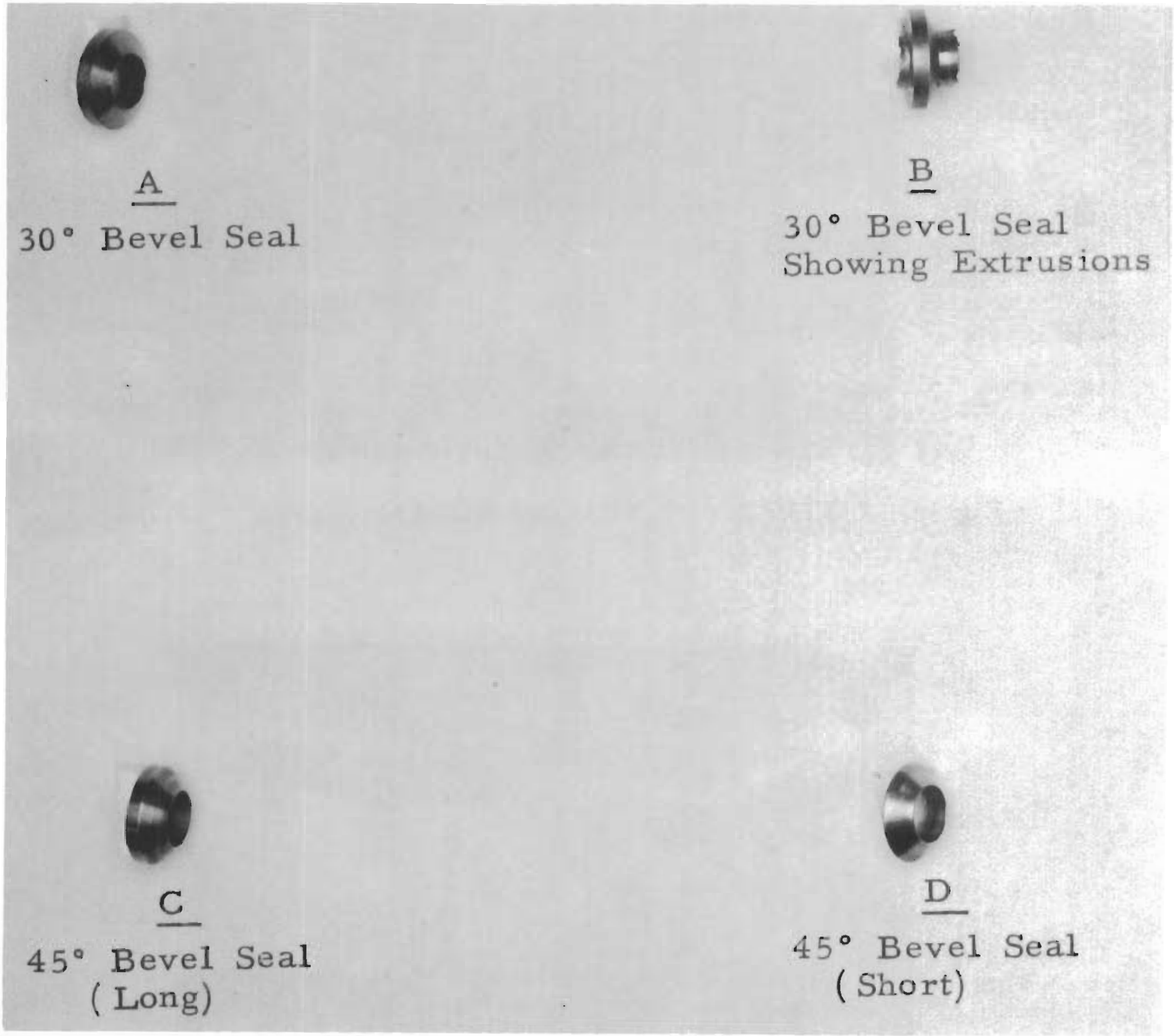


Fig. 22 TYPES OF SEALS USED IN ROTATING SHAFT ELASTOMERS

All of the seals of Fig. 22 were 7/16-inch O.D. and 1/4-inch I.D. and were made of a bonded stainless steel skeleton, 23 per cent density, filled with a 16 per cent indium, 84 per cent silver composition. Seal "C" is a typical seal employing a 45° bevel, which was used with the new stuffing box and gland mentioned above. Difficulty was still experienced in achieving a satisfactory seal, so a shorter seal, indicated as "D" in the photograph, was made. This seal, which required less torque on the gland nut for a given degree of sealing, was not completely tested because of difficulties with the shafting.

The shafts tried are shown in Fig. 23. The shaft marked "A" was made of No. 303 stainless steel, had a hardness of 23 Rockwell C, and was scored by the metal fiber ends of the seal. Shaft "B" was made of No. 440 c stainless steel, hardened and ground, with a hardness of 56 Rockwell C. This shaft was burnished rather than scored by the seal. However, when rotation was started while the fixture was under hydraulic pressure, seizure between the shaft and the stuffing box occurred at the land area. The same thing happened when a hard chrome plated shaft "C" was rotated and hydraulic pressure was introduced. It was theorized that a foreign particle, such as a piece of metal fiber, had lodged between the shaft and stuffing box land and may have caused the seizure.

Since difficulties were still evident with the rotating shaft fixture, further investigation should be carried out, as follows:

1. Determine the optimum clearance between shaft and stuffing box land so neither extrusion of the seal nor seizure occurs.
2. Try Belleville washers to see if they improve the wear adjustment qualities of the seal.
3. Improve the finish on the seals so they appear smooth under a microscope.

VII. RADIATION EFFECTS

Since some of the materials used on this program appear to be promising, it was thought desirable to conduct a preliminary investigation of the effect of radiation on these materials.

The principal types of radiation which affect seal materials are beta particles, which are electrons (negative charges), gamma rays, which are electromagnetic waves of photons with no charge and negligible mass, and neutrons, which have no charge and a mass nearly that of the proton.

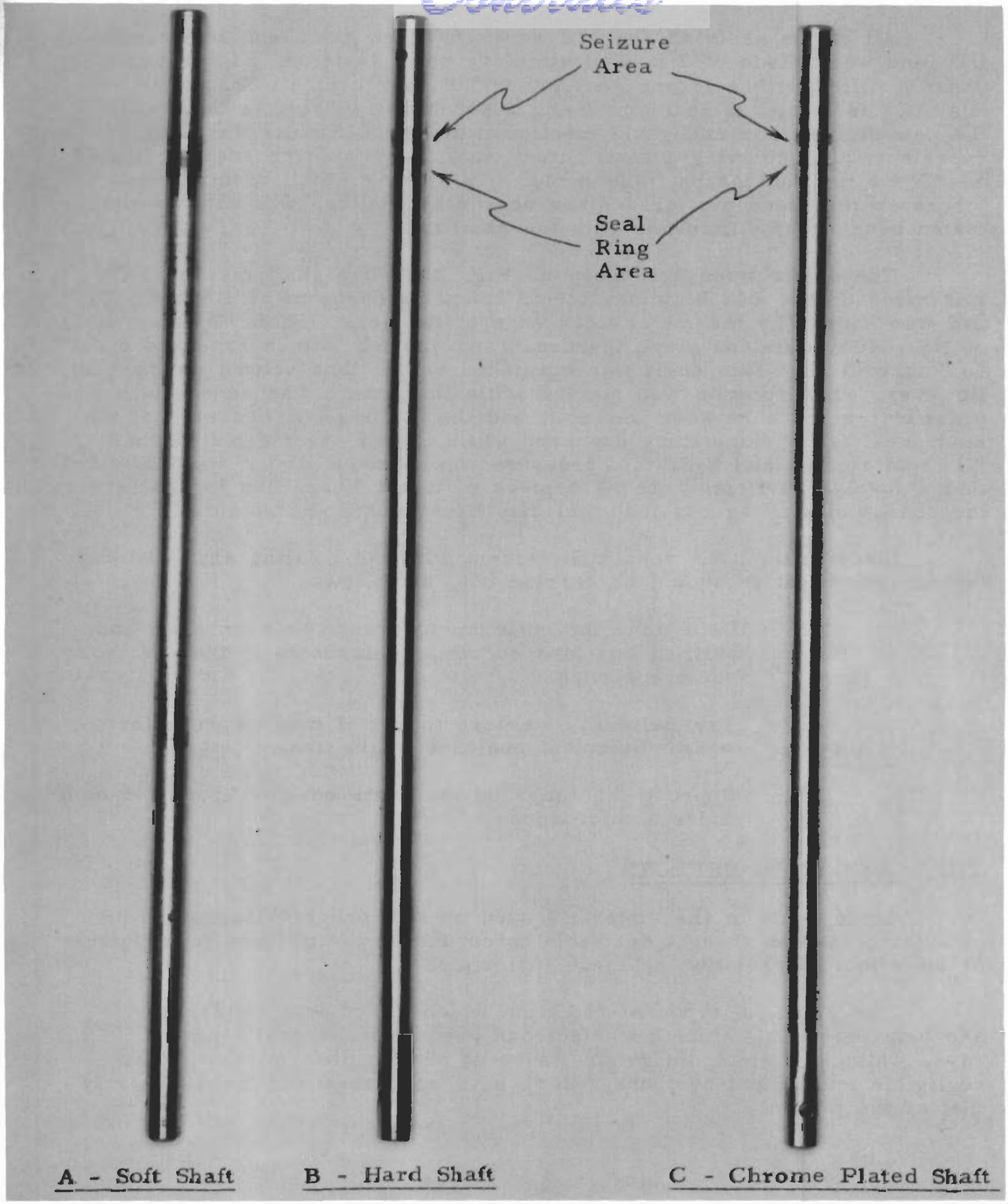


Fig. 23 SHAFTS USED WITH ROTATING SHAFT FIXTURE

Metallic solids are mainly affected by neutron radiation. The effect of beta and gamma radiation on metals is negligible. The neutrons act to displace atoms from equilibrium positions in crystal lattices and thus change the physical properties of the metal, as indicated by Table 11.

Other promising metals for seal applications are silver and indium, which have been used for control rods because of their capacity to absorb large amounts of neutrons. This capacity leads to the reasonable assumption that more changes take place in these lattice structures than in those of Table 11. The changes in mechanical properties would be likely to follow the trend shown in Table 11, but the extent of the changes depend on such factors as the proportion of fast neutrons to thermal neutrons, the total amount of radiation, etc.

Polymers are generally affected by beta, gamma and neutron radiation and the damage to these materials is caused by ionization. This is often created by a neutron being captured by an atom which then acquires a high energy level. This atom strongly interacts with the other atoms of the lattice, producing intense ionization along the way. Table 12 shows the radiation stability of some high-temperature polymers.

VIII. CONCLUSIONS

Under the present contract with the Materials Central of WADD, a systematic approach has been taken toward the development of suitable materials for extreme temperature seals. In the period covered by the Part I summary report, the emphasis was placed on determining the existing state of the art, on fabrication techniques, on mechanical properties, and on screening likely candidates.

As the result of work done during the period covered by the Part II summary report, the value of composite materials developed by Armour for static seals was determined. Republic Aviation reported[1] that a silver-molybdenum fiber crush washer was evaluated for 93 hours without leakage, including repeated disassembly and reassembly. This included about 66 hours at 1000°F, and almost 239,000 pressure cycles from 50 to 4000 psi. Also, Armour has evaluated the same material as a static hot air seal from room temperature to 1200°F with repeated cycling from zero to 5000 psi with no leakage detected, as mentioned previously in this report.

During the period covered by this summary report, advances were made in dynamic sealing applications which carried the composite concept forward into a more complex area. In the early part of this report the results of reciprocating tests at high temperatures by Republic Aviation and the results of static tests at cryogenic temperatures by the National Bureau of Standards were given. At Armour various studies were conducted

---

[1] Republic Aviation Bi-Monthly Progress Report No. 6 - Phase II, 10 May 1960, "Design and Development of a 1000°F Hydraulic System", Contract AF 33(616)-6411.

Table 11

CHANGE IN MECHANICAL PROPERTIES OF METALS AND ALLOYS[1]

Metals	Properties	Exposure	Change Observed	Remarks
Type 304 SS	Hardness	1.3 x $10^{19}/cm^2$ thermal neutrons, $10^{18}/cm^2$ fast neutrons	Negligible	200°C during exposure
	Fatigue strength	2 x $10^{19}/cm^2$ fast neutrons	Insignificant	Irradiated at 100°C tested at 1700 cpm
Type 316 SS	Hardness	5 x $10^{19}/cm^2$ fast neutrons	83 ⟶ 98 R_B	Exposed at 25°C
	Ultimate strength	5 x $10^{19}/cm^2$ fast neutrons	+ 90 per cent	
	Elongation at rupture	5 x $10^{19}/cm^2$ fast neutrons	- 15 per cent	
Molybdenum	Hardness	$10^{20}/cm^2$ fast neutrons	+ 35 Brinell numbers	Exposed at 80°C
	Yield strength (2 per cent offset)	$10^{20}/cm^2$ fast neutrons	100,000 ⟶ 140,000 psi	Exposed at 80°C
	Fracture strength	$10^{20}/cm^2$ fast neutrons	220,000 ⟶ 160,000 psi	Exposed at 80°C
	Ductile-to-brittle transition temperature	$10^{20}/cm^2$ fast neutrons	-30 ⟶ +70°C	Exposed at 80°C

---

[1] Nuclear Engineering Handbook, Harold Etherington, Editor, McGraw-Hill, New York, 1958

Table 12

RADIATION STABILITY OF ELASTOMERS AND PLASTICS USED AS SEALS AND GASKETS FOR OPERATION ABOVE 300°F [1]

Material	Chemical Composition	Temperature Range, °F	Radiation Stability in Listed Environment, Maximum Dosage, ergs g^{-1} (C)	Remarks
Viton /A	Copolymer of hexafluoropropylene and vinylidene fluoride	-65 to 600	1×10^{18} in diester oil at 400°F 6×10^{9} in air at room temperature	Tensile strength decreased by 75 per cent when exposed to 5×10^{8} ergs g^{-1} (C) at 400°F in argon gas
Kel-F Elastomer	Copolymer at chlorotrifluoro-ethylene and vinylidine chloride	to 400°F	$<6 \times 10^{8}$ at room temperature	Becomes soft and tacky
Silicones				
SE 551 (white)	Polymethylphenylsiloxane	-70 to 450	1.34×10^{9} in air at room temperature as samples	Broke when handled at 8.3×10^{9} ergs g^{-1} (C)
Silastic 181	Polydimethylsiloxane		2×10^{11} as vacuum seal at room temperature	Did not hold at 3.7×10^{11} ergs g^{-1} (C)
Teflon	Polytetrafluoroethylene	to 500°F	$<2.7 \times 10^{8}$ in air at room temperature	Crumbled at 8.3×10^{8} ergs g^{-1} (C). Felted Teflon holds seal better than solid Teflon

---

[1] The Effect of Nuclear Radiation on Seals, Gaskets, and Sealants, Technical Memorandum No. 8, Battelle Memorial Institute, Contract 33 (616)-5171, Task No. 60001, Project No. 2133 (AF), November 30, 1958

with emphasis on dynamic developments such as sealing concepts for rotating and reciprocating shafts.

Although much work remains to be done, it is concluded that the concept emphasized throughout the program, namely combining the desired qualities of several materials by means of composites, shows signs of being a fruitful one.

IX. RECOMMENDATIONS FOR FUTURE WORK

Future effort should be concentrated on materials and composite systems for both static and dynamic conditions with the temperature range extended to cover -423°F to 1500°F and with pressures up to 5000 psi. Some specific areas of research are recommended below.

1. Development of new resilient composite materials. Since there is a need for low pressure, low clamping force seals, other metallic and non-metallic fibers and fillers should be studied with this in mind.

2. Metal fiber studies should be conducted with the aim of optimizing the fiber thickness, length, configuration, and arrangement of fibers.

3. Skeleton materials other than those presently being investigated will be evaluated in a search for materials which will give greater strength and resilience at cryogenic and extremely high temperatures.

4. Metal impregnants should be studied to optimize combinations of materials. For example, the use of silver and indium at 1500°F is questionable since this approaches the melting point of silver and a sharp degradation in physical properties may occur. Therefore the possibility of using dispersion hardened silver, and the addition of fine particles of graphite or $Al_2 0_3$ to silver should be investigated.

5. Seal applications should be carried forward, with emphasis on development of seals for rotating and reciprocating shafts.

6. Wherever possible, a basic or theoretical approach should be used to supplement and direct the experimental work. For example, a better understanding of the factors which affect sealing at extreme temperatures would do much in directing developmental work.

BIBLIOGRAPHY

1. Broadway, N. J., and Palinchak, S., "The Effect of Nuclear Radiation on Seals, Gaskets, and Sealants", Technical Memorandum No. 8, Radiation Effects Information Center, Battelle Memorial Institute, Columbus, Ohio, November 30, 1958

2. Drummond, W.W., and Roth, W.P., "Research and Development on Low-Fluidity Refractory Materials", Bjorksten Research Laboratories, Inc., Madison, Wisconsin

3. Ference, Michael, Jr., "Effects of Radiation on Materials", Presented at the SAE Annual Meeting, Detroit, Michigan, January 14-18, 1957

4. Kumpitsch, R.C., "Research on Liquid Metals as Power Transmission Fluids", General Electric Company, Light Military Electronics Department, Wright Air Development Division Progress Report Nos. 5 and 6

5. Lee, J., "High Temperature Hydraulic Evaluation Program", Progress Report No. 14, Republic Aviation Corporation, Farmingdale, Long Island, New York

6. "Materials in Space Environment", Proceedings of the Fifth Sagamore Ordnance Materials Research Conference, PB 151900, United States Department of Commerce Office of Technical Services

7. Mayhew, W.E., "Design and Development of a 1000°F Hydraulic System", Republic Aviation Corporation, Farmingdale, Long Island, New York

8. Nuclear Engineering Handbook, Harold Etherington, editor, McGraw-Hill, New York, 1958

9. "Nuclear Reactors Pose New Problems in Mechanical Design", General Electric Company and American Machine and Foundry Corporation, Product Engineering, April 1956, pp. 187-210

10. Seegman, I.P., et al, "Development of High Temperature Sealants", Wright Air Development Division Technical Report 58-89, Part II, September 1959, Products Research Company

11. Siebert, Raymond A., "The Effect of Nuclear Raidation on Sealants", Materials Research and Process Engineering, Douglas Aircraft Company, Inc., Engineering Paper No. 893, October 1959

12. Trepus, G.E., et al., "Design Data for "O"-Rings and Similar Elastic Seals", Boeing Airplane Company, March 1960, Wright Air Development Division Technical Report 56-272, Part V.

APPENDIX I

COMPARATIVE FRICTION MEASUREMENT APPARATUS

Temperature constitutes the most important factor under which two sliding surfaces must operate. Two sliding surfaces are encountered in a reciprocating shaft seal arrangement. A device imitating such movements under load and temperature conditions was constructed for the purpose of studying material friction and wear properties under controlled conditions, before an actual seal is made.

The design and arrangement of this device is shown schematically in Fig. 24. The material specimen is stationary and is pressed against the vertical sliding surface with a screw through a calibrated spring. The magnitude of this normal load "N" is measured by the amount of spring deflection. The specimen is 1/4-inch in diameter and 3/8-inch long.

A vertically moving member is supported by two pairs of rollers. One end of this member is connected to the friction force "F" measuring component which in turn is connected to the reciprocating rod of the air cylinder.

The stroke is adjustable over a range of 4 inches. Also, the frequency of the motion is adjustable.

The electric heater is made of two halves and is mounted on a hinge to provide easy specimen placing. Controlled temperature up to 1200°F can be obtained. The actual temperature of the specimen was measured by placing a thermocouple junction near the sliding surface. The other components and the functioning of the set-up is self-explanatory from the sketch.

During the experimental evaluation, breakaway and sliding friction are measured. The force which acts between two bodies at their surface of contact, so as to resist their sliding on each other, is generally defined as friction or resistance to motion. The relation between force of friction and normal pressure is given by the coefficient of friction, denoted by the Greek letter μ. Thus $F=\mu N$ or $\mu=F/N$.

A greater force is required to start a body from a state of rest than to merely keep it in motion because the friction of rest or breakaway is greater than the friction of motion. Every material exhibits different friction properties. Materials having lower friction are better suited for dynamic seal applications. Therefore, this property is used as a yardstick to screen various materials under development.

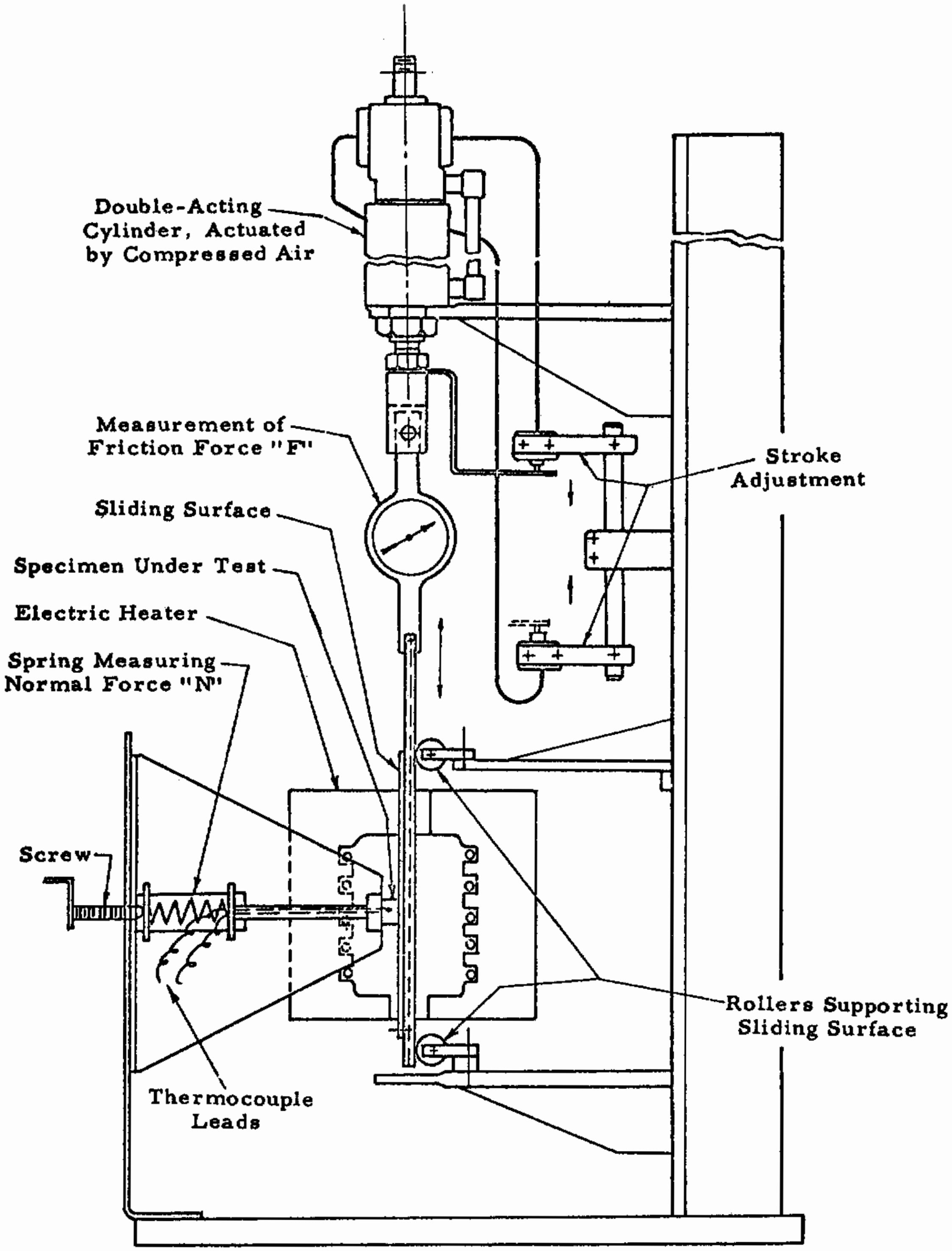


Fig. 24 COMPARATIVE FRICTION MEASUREMENT APPARATUS

The friction values measured were higher than what the actual value would be and are called comparative because the rolling friction of the moving member was not accounted for separately. The apparatus shown in Fig. 24 was used to study friction and wear properties of various material combinations. Experimental data are presented in Appendix II, and elsewhere.

Before a material is accepted for seal use, it must, in addition to possessing favorable physical properties, be capable of being fabricated into desired seal configurations. The final test is, of course, its ability to seal when subjected to conditions simulating the actual environment in which it is to operate.

APPENDIX II

FRICTION AND WEAR DATA

Table 13

FRICTION AND WEAR CHARACTERISTICS OF TALC MATERIALS COMPACTED WITH VARIOUS BINDERS

Test Conditions: 1200°F, 80 psi pressure against moving plate, 55 ft/min average rubbing velocity, 5 minutes total running time

Sample No.	Composition, Weight Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
1	77 talc 23 Nalcoag	Too soft	Crumbles rapidly to powder		
2	66 talc 34 Potassium Silicate	1.2	0.0002	4	A few deep scores in plate. Some sticking of the sealant to plate.
2A	66 talc 34 Sodium Silicate	1.3	0.0002	5	Deep scores in plate
3	65 talc 35 teflon dispersion	Evaluated at 450°F.	Sealant deforms and tears apart.		
4	77 talc 23 aluminum phosphate liquor	22.4	0.016	7	Sealant is mechanically strong but wears rapidly. Plate was badly scored.
5	21 talc 63 Glass No. 461 16 Nalcoag	16.5	0.013	10	Some tendency for sealant to stick and stall movement of plate. A few scores in plate.
6	10 talc	0.21	0.00008	6	Smoothly running assembly. Thin, adherent film of sealant on plate. Only a trace of scoring. Sealant has polished appearance.

Table 14

FRICTION AND WEAR CHARACTERISTICS OF VARIOUS MATERIALS

Test Conditions: 1200°F, 80 psi pressure against moving plate, 55 ft/min average rubbing velocity, 5 minutes total running time

Sample No.	Composition, Weight Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
7	40 boron nitride 60 potassium silicate	47.5	0.073	3	Sealant too soft or weakly bonded. High wear rate. Plate not scored.
7A	commercial hot pressed boron nitride	56.5	0.043	2	Rapid sealant wear. Plate not scored.
8	9 boron nitride 79 Glass No. 461 12 Nalcoag	21.2	0.015	3	Rapid sealant wear. Plate not scored.
9	10 boron nitride 90 silver	43.6	0.020	4	Rapid sealant wear. Plate not scored.
10	62 mica 38 potassium silicate		0.15		Very rapid sealant wear
11	9 mica 79 Glass No. 461 12 Nalcoag	.98	0.0012	10	Plate lightly scored. Sealant slightly worn.
12	9 mica 82 silver 9 Nalcoag	.72	0.0009	6	Slight scoring of plate. Sealant has polished appearance.
13	62 fibrous potassium titanate 38 potassium silicate	63.8	0.042	6	Rapid sealant wear. Some scoring of plate.
14	79 lead fluoride 21 potassium silicate	Silicate and fluoride flux to form low melting material. Not suitable for 1200°F operation.			

Table 14 (cont'd)

FRICTION AND WEAR CHARACTERISTICS OF VARIOUS MATERIALS

Sample No.	Composition Weight, Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
15	67 lead oxide 33 potassium silicate	Suitable body not formed due to severe shrinkage and vitrification on firing to 1200°F			
16	9 graphite 78 Glass No. 461 13 Nalcoag	2.1	0.004	8	Sealant buildup on plate. Some scoring. Noticeable loss of graphite with sustained heating.
17	7 moly. disulfide 72 Glass No. 461 21 Nalcoag	11.3	0.009	10	Noticeable thermal decomposition of molybdenum disulfide. Some scoring of plate.
18	9 talc 9 lead oxide 73 silver 9 Nalcoag	0.01		6	Sealant flattened and deformed under test load. Wear measurement, therefore, not obtained. Only a trace of scoring on plate.
19	9 graphite 87 lead oxide 4 Nalcoag	Graphite burned out and structure collapsed at 1200°F			
20	62 talc 19 lead oxide 19 potassium silicate	0.65	0.0005	8	Deeply scored plate.
21	64 talc 13 lead oxide 2 lead fluoride 4 graphite 17 potassium silicate	2.5	0.003	9	Considerable scoring of plate
22	7 talc 3 mica 79 silver 11 Nalcoag	0.41	0.0002	9	Plate slightly scored. Sealant is polished.
23	All silver body	0.04		6	Sealant deformed under test load. Wear measurement not obtained. A trace of scoring on plate.

Table 14 (cont'd)

FRICTION AND WEAR CHARACTERISTICS OF VARIOUS MATERIALS

Sample No.	Composition Weight, Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
24	Sapphire	0.70	0.001	7	Plate deeply scored
25	9 talc 83 lead 8 Nalcoag	10.7	0.007	4	Sealant rather weakly bonded. Noticeable oxidation of the lead. No serious scoring of plate.
26	12 talc 80 copper 8 Nalcoag	0.44 wt. gain	0.00008	4	Noticeable oxidation of copper. Sealant has glossy polish. Very light, almost no scoring of plate.
27	8 talc 8 zinc oxide 62 silver 22 potassium silicate	3.5	0.002	6	Deeply scored plate
28	72 zinc oxide 28 potassium silicate	Sealant stuck to plate and broke off. Apparently, must have high breakaway friction. Sample is hard but wears rapidly.			
29	77 chrome oxide 23 potassium silicate	6.1	0.003	4	Some scoring of plate
30	59 talc 15 Glass No. 461 26 potassium silicate	0.23	0.002	5	Deeply scored plate. Deposit on sealant.
31	69 ball clay 31 potassium silicate	High breakaway friction. Sample broke.			
32	Coating of "Solution Ceramic" Alumina on steel substrate		Coating quickly rubbed off. Plate deeply scored.		
33	Coating of "Solution Ceramic" Chromia on steel substrate		Same as No. 32		
34	Coating of "Solution Ceramic" Zirconia on steel substrate.		Same as above		

Table 14 (cont'd)

FRICTION AND WEAR CHARACTERISTICS OF VARIOUS MATERIALS

Sample No.	Composition Weight, Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
35	77 aluminum phosphate powder 23 water		Mechanically weak structure		Very rapid sealant wear
36	59 boron phosphate 18 talc 23 potassium silicate		Very rapid sealant wear		
37	22 Fiberfrax 56 talc 22 potassium silicate		Very rapid sealant wear		
38	50 cadmium sulfide 33 talc 17 potassium silicate	1.0	0.0007	8	Plate polished. Sealant polished. No apparent scoring of plate
39	37 cerium oxide 37 talc 26 potassium silicate	0.95	near zero	5	Considerable scoring of plate. Deposit on sealant.
40	56 thorium oxide 11 talc 33 potassium silicate	1.9	0.0005	5	Plate scored. Deposit on sealant.
41	56 calcium fluoride 11 talc 33 potassium silicate	1.9	0.002	4	Plate lightly scored
42	31 aluminum 31 talc 38 potassium silicate		Sealant bloated on firing.	Too friable and weak for evaluation.	
43	53 magnesium oxide 16 talc 31 potassium silicate	5.4	0.002	5	Plate deeply scored

Table 14 (cont'd)

FRICTION AND WEAR CHARACTERISTICS OF VARIOUS MATERIALS

Sample No.	Composition Weight, Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
44	74 wollastonite 26 potassium silicate	3.6	0.002	6	Plate deeply scored
45	50 barium sulfate 25 talc 25 potassium silicate	0.66	0.0004	4	Plate lightly scored. Some polishing of sealant.
46	80 zinc sulfide 20 potassium silicate		Plate deeply scored. Sealant broke in testing.		
47	84 bismuth oxide 8 talc 8 potassium silicate	0.41	0.0007	6	Plate scored
48	7 cadmium sulfide 7 talc 65 silver 21 potassium silicate	0.01 wt. gain	0.0002	6	Smooth operation. Plate polished. Sealant polished. No apparent scoring
49	40 phthalocyanine 30 talc 30 potassium silicate		Very rapid sealant wear. Body grinds to powder.		
	room temperature evaluation	0.002	0.0001	2.5	Sealant polished. No scoring of plate.
50	25 talc 58 silver 17 potassium silicate	0.34	0.0002	6	Plate deeply scored
51	67 lead sulfide 13 talc 20 potassium silicate	0.20	0.0006	5	Sealant polished. Light scoring of plate.
52	77 zircon 12 talc 11 potassium silicate	2.4	0.002	5	Plate deeply scored. Deposit on sealant

Table 14 (cont'd)

FRICTION AND WEAR CHARACTERISTICS OF VARIOUS MATERIALS

Sample No.	Composition Weight, Per cent	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
53	59 titanium oxide 12 talc 29 potassium silicate		0.001	5	Plate deeply scored. Some chipping of sealant.
54A	67 Pyrex glass 3 mica 3 talc 27 potassium silicate	2.7	0.0006	4	Plate deeply scored. Deposit on sealant.
54B	59 Pyrex glass 6 mica 6 talc 29 potassium silicate				Plate deeply scored. Sample broke in testing.
54C	50 pyrex glass 10 mica 10 talc 30 potassium silicate	11.1	0.008	6	Plate scored. Rapid sealant wear.
54D	20 Pyrex glass 20 mica 20 talc 40 potassium silicate		Very rapid sealant wear		
55	80 talc 20 silicone SR-32	25.1	0.02	5	Evaluated at 500°F. Very rapid sealant wear. No scoring of plate.
56	72 chromium 14 talc 14 potassium silicate	8.4	0.0001	5	Plate deeply scored
57	82 nickel 9 talc 9 potassium silicate	1.1	0.0004	4	Plate lightly scored
58	77 iron 8 talc 15 potassium silicate	1.4	0.0003	6	Plate deeply scored

Table 15

ADDITIONAL EVALUATION OF THE BETTER COMPOSITIONS AT 1200°F

Sample No.	Composition, Weight, Per cent	Running Time, min	Rubbing Speed, ft/min	Load on Specimen, psi	Weight Loss, Per cent	Wear Rate, in./min	Breakaway Friction, lb	Remarks
6	10 talc 90 silver	15	65	80	0.15	.0001	6	Sealant has glossy polish. No apparent damage to plate.
6		5	55	160	Sealant deformed and finally broke under the increased load. A trace of scoring on plate.			
26	12 talc 80 copper 8 Nalcoag	15	65	80	0.25 wt. gain.	.00003	6	Sealant polished. Some scoring and buildup on plate.
26		5	55	160	Loud squeaking noise. Sealant chipped and broke. Plate scored.			
38	50 cadmium sulfide 33 talc 17 potassium silicate	15	65	80	1.3	.0002	6	Sealant polished. Some scoring of plate.
38		5	55	160	6.9	.005	10	Plate scored. Noticeable sealant wear.
48	7 cadmium sulfide 7 talc 65 silver 21 potassium silicate	15	65	80	0.03 wt gain	.0002	6	Sealant polished. No scoring.
48		5	55	160	near zero	.0002	7	A trace of scoring
51	67 lead sulfide 13 talc 20 potassium silicate	15	65	80	0.10	.0002	5	Slightly scored plate