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IMPROVED HIGH-TEMPERATURE PERCUSSION PRIMER

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ABSTRACT

A study was conducted to develop a percussion primer mix that would be capable of functioning after a 20-hour exposure at 200°C. A total of 16 mixes were studied, of which 6 were chosen for basic thermal and chemical properties. All mixtures were thermally evaluated with the differential scanning calorimeter (DSC) and showed no exothermic activity below 250°C. The mixtures were further evaluated by impact and friction sensitivity. Two of the candidate mixtures were selected for further development of a high-temperature, hermetically sealed percussion primer. These were $KClO_3/Sb_2S_3/CaSi_2$ and $KClO_3/Sb_2S_3/CaSi_2/HNS$. The primer mixes were loaded into conventional hardware and subjected to ball-drop sensitivity testing. These two mixes have similar mean sensitivity of approximately 30 in. oz. which are well within the design requirements of 60 in. oz. The hermetically sealed primer that is being developed uses a stainless steel cup, anvil, and sealing ring with a glass-to-metal seal in the output hole. This primer has no reconsolidation requirements, and the sensitivity of this percussion primer is comparable with other commercial primers which are not hermetically sealed.

INTRODUCTION

Work on high-temperature percussion primers has been going on since 1961 when Schlach & Ciccone of the Frankford Arsenal developed the first pyrotechnic mixes capable of functioning after exposure to 400°F (200°C).[1,2] These mixes, G-11 and G-16, were slurry loaded into standard brass hardware, then dried. This method requires that the primers be recompacted in the final application. Under most circumstances, this requirement is not detrimental. These high-temperature primers used the standard paper disc seal between the mix and the anvil. This seal is not an effective barrier in controlling moisture exposure to the mix. It has been shown that improper consolidation and moisture are the major factors affecting percussion primer sensitivity.[1,2,3]

In an attempt to address these problems, B. F. Beard of the Naval Ordnance Station developed a Cartridge Activated Device (CAD) primer[3], which had no consolidation requirements and an improved environmental seal. This device is made of copper alloys and has a flat anvil design, improving off-center hit sensitivity (Figure 1). The CAD primer is more sensitive than the "G"-type primers; however, its temperature stability is lower. The CAD primer has an upper temperature limit of 200°F (100°C).

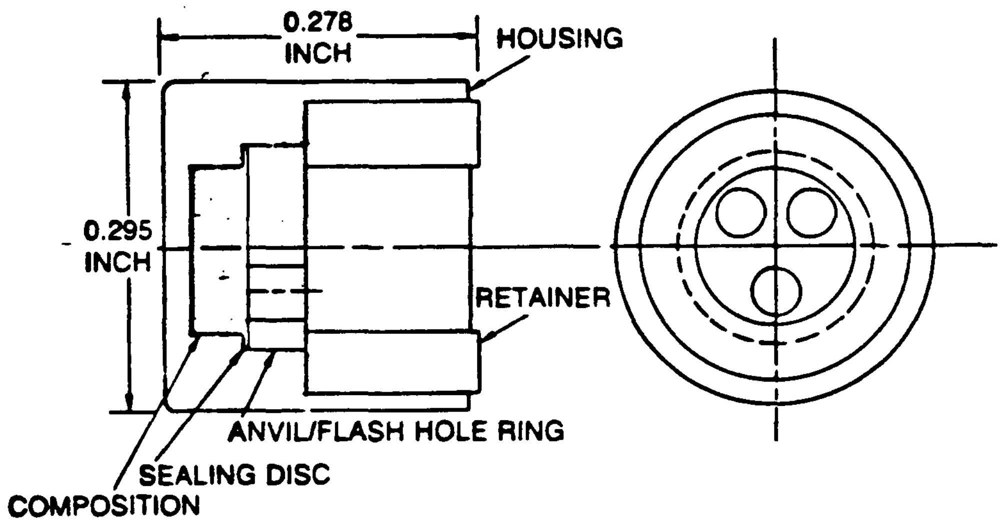

Figure 1. CAD Primer Basic Design

Our objectives were to develop a hermetic high-temperature (200°C, 400°F) percussion primer with an all-fire sensitivity of less than that of the "G" primers and maintain the CAD primer advantages of no reconsolidation and a flat anvil.

PREPARATION AND EVALUATION OF PRIMER MIXES

Sixteen compositions were formulated after studying their basic thermal and chemical properties. The formulations are presented in Table I. The mixes were examined for thermal stability using differential scanning calorimetry (DSC). None of the mixes show any thermal activity below 250°C. Further evaluation of the impact and friction sensitivity was conducted. These results are presented in Table I. The impact sensitivity was conducted using a (2 Kg) Bureau of Mines apparatus. The friction sensitivity was measured using a BAM Friction Test Apparatus. The values reported are the minimum weight required to give one fire in six attempts.

Mixtures 1 through 10 were blended by weighing 5 grams total weight of dry ingredients into a 2-inch-diameter by approximately 2-inch-long can. Two 1/2-inch-diameter, 1-inch-long velostat rods were added, and the can was rotated at 30 rpms for 18 hours. Compositions using BI-770 were blended in small amounts due to its sensitivity. Mixture number 11 was blended by crushing the materials together on a piece of paper with a wooden spatula. Mixture number 16 was prepared by grinding a small amount of mixture number 5 with BI-770 and a few drops of water.

Six mixtures were chosen to load into M42 brass hardware for further impact testing. These results are presented in Table II.[4] Of the six, only three would reliably function at moderate impact energies. They are the G-16 mix, the G-11 (with HNS replacing TACOT), and the G16/BI-770. These mixtures were further tested to establish a mean impact sensitivity using a Langlie format. The results are presented in Table III.[5] During this testing it was observed that the G11/HNS mixture gave the most reliable output. The G-16 output tended to smoke and fizzle at marginal input energies. The G-16/BI-770 mix proved to be too brisant for our application.

TABLE I
PRIMER MIX COMPOSITIONS

	Composition Number															
	1	2	3	4	5	6	7	8	9*	10	11	12**	13	14***	15	16
Potassium Chlorate	40	30	40	53	53	36	42	53	53	50	53	53	53	--	--	42
Antimony Sulfide	--	--	--	25	30	--	--	30	25	--	25	30	17	10	--	24
Calcium Silicide	10	--	10	12	17	--	8	17	12	--	12	17	--	--	--	14
Titanium Metal Powder	15	20	15	--	--	16	8	--	--	40	--	--	--	--	--	--
CC[1]	35	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
TMAP[2]	--	50	35	10	--	18	--	--	--	--	--	--	--	--	--	--
HNS	--	--	--	--	--	--	42	--	--	--	--	--	--	--	--	--
HNSIIB	--	--	--	--	--	--	--	--	--	--	10	--	--	--	--	--
T-TACOT[3]	--	--	--	--	--	--	--	--	10	--	--	--	--	--	--	--
Lead Styphnate (Basic)	--	--	--	--	--	--	--	--	--	--	--	--	--	53	--	--
Barium Nitrate	--	--	--	--	--	--	--	--	--	--	--	--	--	22	--	--
Aluminum (Powdered)	--	--	--	--	--	--	--	--	--	--	--	--	--	10	--	--
Tetracene	--	--	--	--	--	--	--	--	--	--	--	--	--	5	--	--
BI-770[4]	--	--	--	--	--	--	--	--	--	10	--	--	--	--	100	20
Lead Thiocyanate	--	--	--	--	--	--	--	--	--	--	--	--	25	--	--	--
TNT	--	--	--	--	--	--	--	--	--	--	--	--	5	--	--	--
Impact Height 2 Kg Bureau of Mines (cm)	70	65	55	75	50	65	35	>100	50	--	--	35	10	40	50	--
Friction Sensitivity BAM (grams)	>1000	>1000	>1000	>1000	900	--	--	>1000	>1000	--	--	750	200	950	100	--
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Notes:

* G-11 Mix

** G-16 Mix

*** M42C1 Mix

1. CC is a coprecipitated mixture of potassium hexacyanocobaltate and potassium perchlorate per UniDynamics Phoenix Document 108-PPR-01.
2. TMAP is tetramethylammonium perchlorate.
3. T-TACOT is tetranitrodibenzo-1,3a,4,6a,-tetrazapentalene.
4. BI-770 is the silver salt of bitetrazole.

Table II

PRIMER MIX LOADED IN BRASS HARDWARE

	Composition	Impact Height[1] (cm)	Results
#3	40% $KClO_4$		
	10% Sb_2S_3	10	No Fire
	15% Ti	20	No Fire
	35% TMAP	30	No Fire
#5	G-16 Blend		
	53% $KClO_4$	10	Fire
	30% Sb_2S_3	10	No Fire
	17% $CaSi_2$	15	Fire
#7	42% $KClO_4$[2]	10	No Fire
	8% $CaSi_2$	20	No Fire
	8% Ti (Metal)	30	No Fire
	42% HNS		
#10	50% $KClO_4$	10	No Fire
	40% Ti (Metal)	20	No Fire
	10% BI-770	30	No Fire
#11	G-11/HNS		
	53% $KClO_4$	10	No Fire
	25% Sb_2S_3	10	Fire
	12% $CaSi_2$	10	Fire
	10% HNS		
#16	42% $KClO_4$	5	Fire
	24% Sb_2S_3	4	Fire
	14% Ti (Metal)	3	Fire
	20% BI-770	2	Fire
		1	No Fire

Notes: 1. 2 Kg Bureau of Mines Impact Tester.
2. This mix was loaded in Design #1.

Table III

LANGLIE SENSITIVITY RESULTS OF PRIMER MIX THAT FUNCTIONED ON IMPACT TESTING

		$\bar{X}$ (in. oz.)	S	$\bar{X}$ + 5S
#5	G-16 Blend			
	53% $KClO_4$	32.2	3.3	48.7
	30% Sb_2S_3			
	17% $CaSi_2$			
#11	G-11/HNS Blend			
	53% $KClO_4$			
	25% Sb_2S_3	33.9	3.3	50.4
	12% $CaSi_2$			
	10% HNS			
#16	G-16/BI-770			
	42% $KClO_4$			
	24% Sb_2S_3	21.8	0.9	26.3
	14% $CaSi_2$			
	20% BI-770			

Table IV shows the results of preliminary compatibility testing using a Chemical Reactivity Test (CRT).[6] The data for the G-11 mix and HNS measured high CO_2 contents following aging at 200°C. The G-16 mix, which is similar to the G-11 mix, measured moderate CO_2 values. The other evolved gases measured moderate to low values. These CO_2 data are somewhat disturbing in that they indicate a potential reaction between the G-11 constituents and HNS. But the trend is not clear because of the absence of corresponding high nitrogen, NO, and N_2O values. These materials would also be evolved if the HNS was reacting. Note that the only source of CO_2, N_2, NO, and N_2O in this mixture was the HNS. In addition, HNS baseline-evolved gases were not measured and compared. These CRT experiments are to be repeated using stainless steel or quartz holders. Baseline tests will also be run on HNS. To measure the stability of the G-11 constituents during high-temperature aging, a free chloride analysis will be performed. This will measure $KClO_3$ degradation in the G-11 mixture as a result of any reaction with HNS. Further work determining the effect of aging on primer sensitivity is also in progress. If a compatibility problem definitely exists, the G-16 mix would be used in the hermetic primer.

Table IV

CRT ANALYSIS OF PRIMER MIXES

	Micrograms of Evolved Gas Per Gram of Sample						
Mix	N_2	CO	NO	CH_4	CO_2	N_2O	H_2O
Blank	19	6	TR*	TR	106	TR	75
Blank	49	3	TR	3	34	TR	35
G-16	78	52	TR	10	707	9	637
G-16 + BI-770	2205	720	0	12	6613	7	3348
G-11/HNS	718	412	380	32	6091	122	1237
G-11/HNS	563	362	33	7	5005	91	956

*Trace - less than one microgram

The sealing disc used in most commercial percussion primers is a Kraft paper. High-temperature stabilizing tests show that the craft paper deteriorates very badly, becoming charred and outgasing appreciably (Table V). Several alternatives were selected and tested in brass hardware using a disc and a washer configuration. The Kapton washer was relatively simple to make and use. The Kapton proved to be stable and compatible to 200°C when in contact with the G-16 mix. The Kel F, Viton B, and Fluorel were not stable at 200°C and were rejected.

Table V

MATERIAL COMPATIBILITY

Mix	Micrograms of Evolved Gas Per Gram of Sample N_2	CO	NO	CH_4	CO_2	N_2O	H_2O
G-16	78	52	TR[3]	10	707	9	637
Viton B	36	44	4	TR	499	0	930
G-16 + Viton B	149	2078	14	23	11048	183	250
G-16 + Viton B	171	3033	0	22	15888	1	929
Paper[1,4]	55	3752	32	4	13628	1	11390
Paper[1,4]	469	2232	0	7	14001	TR	13630
Kapton[1]	25	164	TR	5	1530	TR	100
Kapton + G-16	303	92	1	6	1033	TR	323
Kapton + G-16	124	81	4	2	641	TR	419
Kel F[2,4]	19	197	0	4.4	1870	TR	415
Kel F + G-16[2,4]	34	508	0	8	4445	2	121
Kel F + G-16[2,4]	41	845	3	12	7246	2	2415
Fluorel[2,4]	83	22	TR	2	234	1	471
Fluorel[2,4]	103	36	TR	3	366	0	774

1. Heated 66 hours
2. Heated 42 hours
3. Trace - less than one microgram
4. Other products detected

THE HERMETIC PRIMER

The hermetic primer requires welding of the final assembly and the use of a sealed spit hole. These requirements were accomplished by using stainless steel for the primer hardware and a glass plug formed in the spit hole of the primer. Several design variations were evaluated using geometries that incorporated the anvil and seals. Other designs were similar to the CAD primer configuration. These designs are shown in Figures 2 through 5. Experiments with these designs were conducted using the G-11/HNS primer mix; the results are presented in Tables VI, VII, and VIII. The results of these experiments show that three factors are involved in reliable function: the primer mix pad thickness, the closure disc or cup thickness, and the glass seal thickness/surface area ratio.

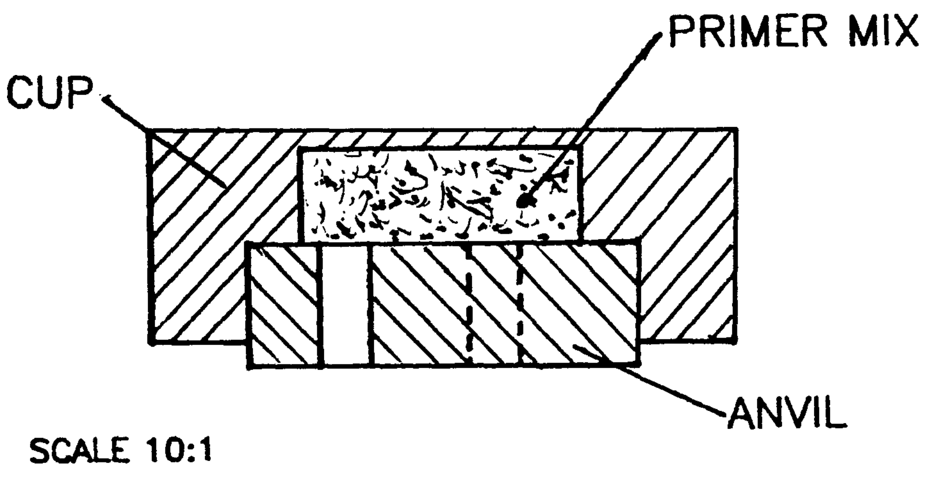

Figure 2. Design 1

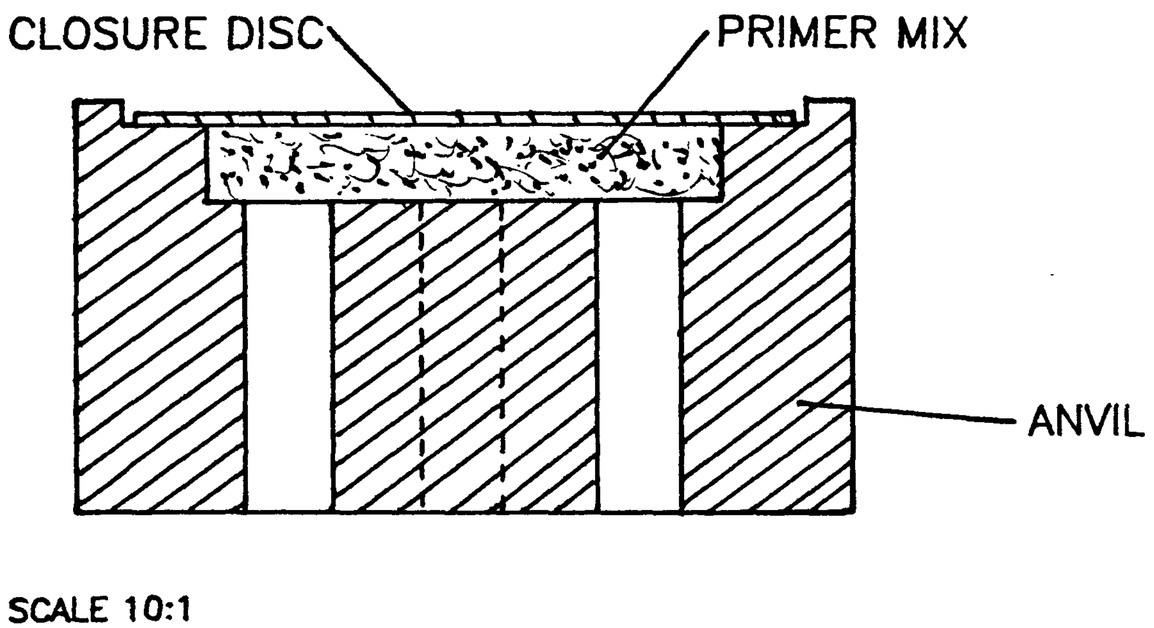

Figure 3. Design 2

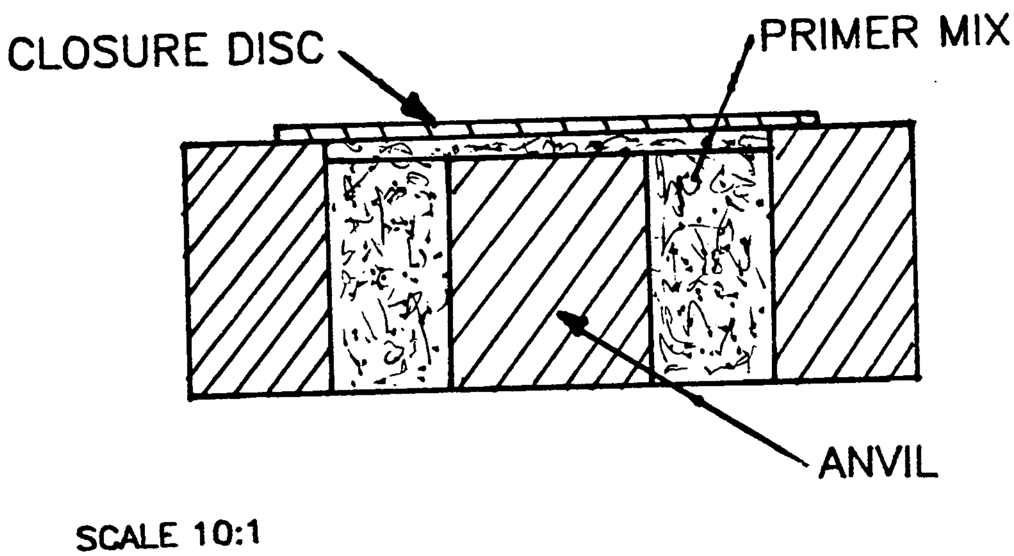

Figure 4. Design 3

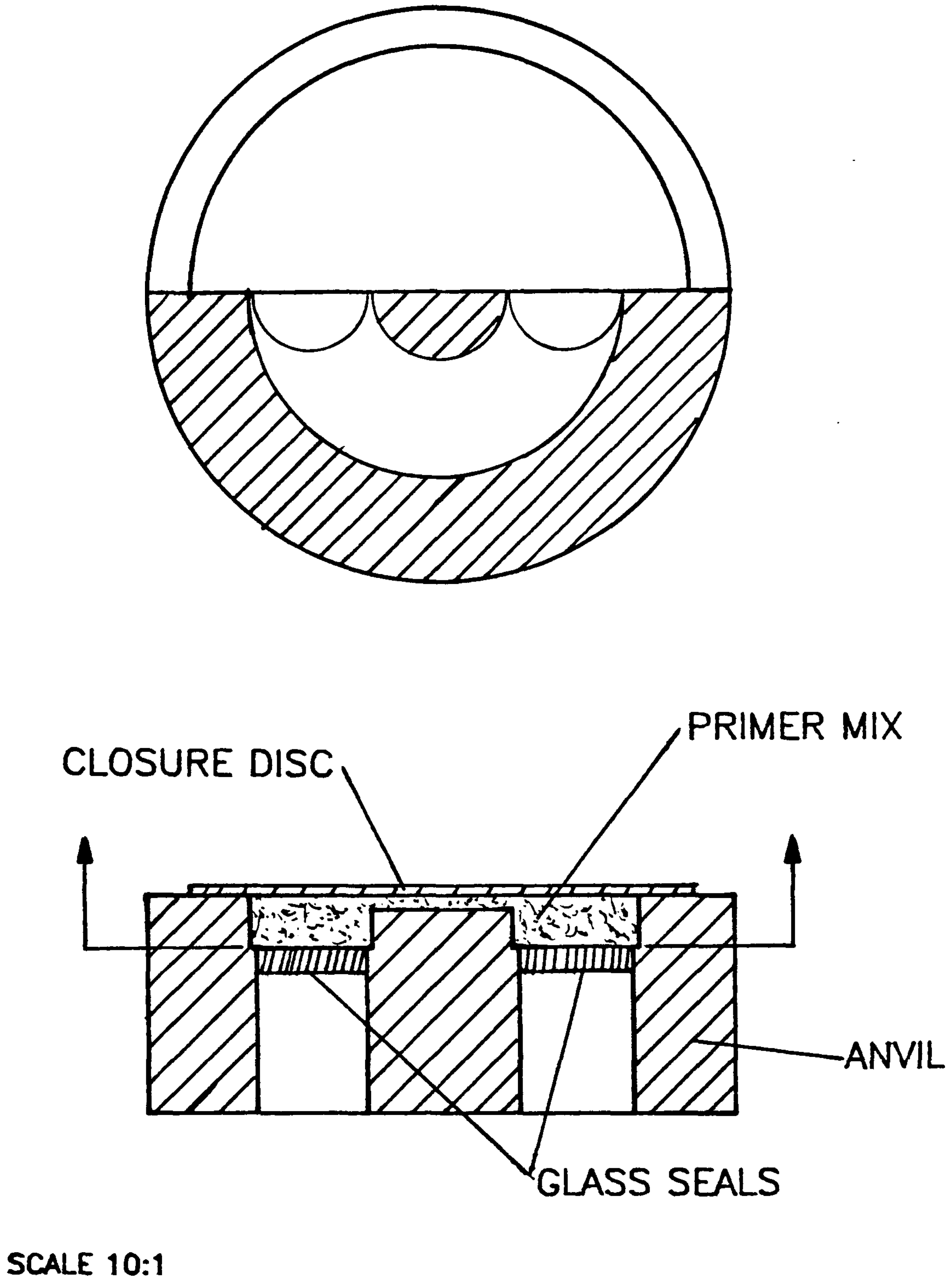

Figure 5. Design 4

Table VI

STAINLESS STEEL HARDWARE DESIGN STUDY

		# Shots	
Design I	.008" Disc .050" Pad	3	No Fires[1]
	.005 Disc .040 Pad	4	2 Fires[1] 2 No Fires
Design II	.005 Disc .020 Pad	3	~50 in. oz.[2]
	.010 Disc .010 Pad	3	~30 in. oz.
	.020 Disc .010 Pad	3	~90 in. oz.
	.005 Disc .010 Pad	3	~20 in. oz.
Design III	.005 Disc .010 Pad .010 Glass Seals	5	~20 in. oz. Failed to rupture
Design IV	.010 Disc .020 Pad .010 Seals	5	~70 in. oz. Seals broke

Notes: (1) 2 Kg Bureau of Mines tester.
(2) Sandia-designed drop tester.

Table VII

PRIMER MIX CONSOLIDATION STUDY

Design IV - .010 Disc

Pad Thickness	% TMD	Sensitivity
.010	60%	~48 in. oz.
.020	60%	~54 in. oz.
.030	60%	~63 in. oz.
.020	75%	~70 in. oz.
.010	90%	~45 in. oz.
.020	90%	~55 in. oz.
.030	90%	~70 in. oz.

Table VIII

GLASS SEAL THICKNESS STUDY

Thickness/Surface Area Ratio	Leak Rate	Results
3.66	$<10^{-7}$	No breakout
2.93	$<10^{-7}$	No breakout
2.43	$<10^{-7}$	No breakout
1.95	$<10^{-7}$	Partial breakout
1.58	$<10^{-7}$	Partial breakout
1.05	$<10^{-7}$	Complete breakout
0.526	$<10^{-7}$	Complete breakout
0.263	$<10^{-7}$	Complete breakout

Final design 0.688   0.136" X .010" thick seal

Table VI shows the cup or disc thickness and primer mix pad thickness effect on the sensitivity of the stainless steel designs. It can be seen that experiments conducted with thick discs/thin pads and thin discs/thick pads result in low sensitivity. The best results were obtained in experiments with thin discs/thin pads. The effect of the primer mix loading densities are presented in Table VII. These results indicate a trend toward increased sensitivity with increased pad thickness, with no apparent density effect. Experiments with the glass seals are summarized in Table VIII. These results show an optimal seal thickness/surface area ratio between 0.5 to 1.0 for this system.

The final hermetic primer design, Figure 6, minimizes the pad and disc thickness while maintaining output and integrity. It also maximizes the seal surface area and maintains hermeticity. This design has a mean sensitivity of 35.91 in. oz. with a standard deviation of 3.78.

Summary

The hermetic high-temperature primer has been developed to withstand extremes of 200°C for 20 hours, which is not normally experienced by commercial percussion primers. This design has incorporated the high-temperature G-11/HNS primer mixture into stainless steel hardware. The hardware maintains the desired features of the CAD primer, i.e., no reconsolidation and flat anvil, and optimizes the sensitivity obtaining a mean of 36 in. oz. The welded assembly with the glass seal provides hermeticity to greater than 1 X 10^{-6} cc/sec.

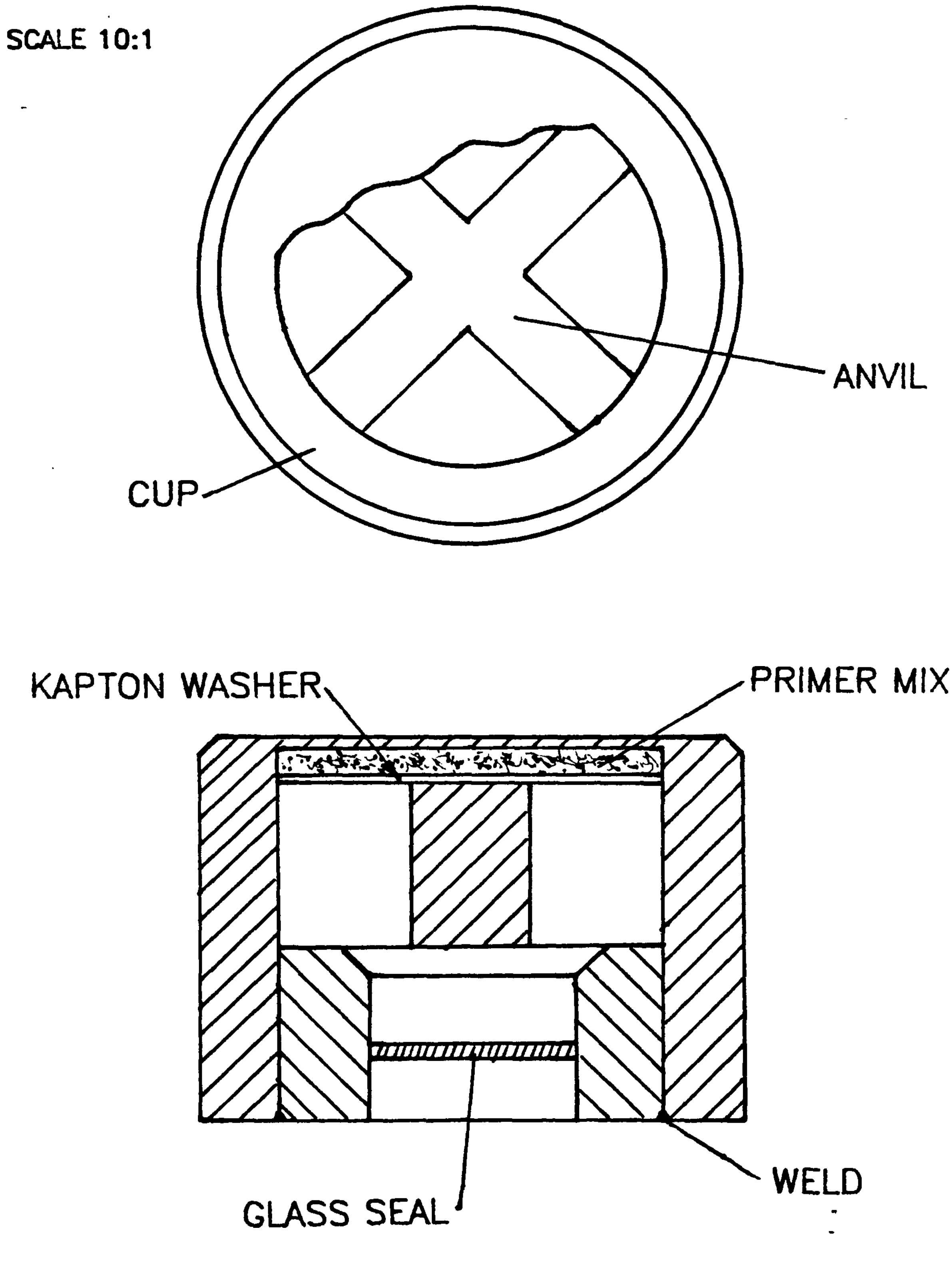

Figure 6. Design 5

References

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3. B. F. Beard, "Advantages of CAD Primers for Air-Crew Escape Systems," Naval Ordnance Station, Proceedings of the Ninth International Pyrotechnics Seminar, Aug. 1984.

4. W. Fleming, unpublished work performed at UniDynamics Phoenix, Inc., under Sandia National Laboratories contract.

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6. L. C. Myers, "The Chemical Reactivity Test - A Compatibility Screening Test for Explosives," American Defense Preparedness Association Symposium on Compatibility of Plastics/Materials with Explosives, May 15-17, 1979, Albuquerque, New Mexico.