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Rock Island Arsenal Laboratory

TECHNICAL REPORT

COMPRESSION SET OF ELASTOMERS AT ELEVATED TEMPERATURES

By

E. W. Bergstrom

Dept. of the Army Project No. 1-H-0-24401-A-111

AMC Code No. 5026.11.843

RIA Report No. 63-798 Copy No.

IEL 1-9-100-5 Date 14 March 1963

The findings in this report are not to be construed as an official Department of the Army position.

"[redacted] Services [redacted]".

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Rock Island Arsenal
Rock Island, Illinois

ABSTRACT

Compression set tests (constant deflection method of ASTM D395-55) were carried out on heat resistant rubber vulcanizates for periods as long as twenty-eight days at temperatures up to 500°F.

It was found that some silicone rubbers did not have set values at elevated temperatures as low as might be expected from their excellent resistance to heat aging.

Cure time was found to have a significant effect on the set of isobutylene/isoprene vulcanizates. Increased cure time resulted in lower set even though the original cure time may have been optimum for other properties.

Certain metal oxide additives significantly lowered the set of some silicones. No one additive was found, however, which lowered the set of all four types of silicones; namely, dimethyl, methyl vinyl, fluoro and high strength. Additives which had been found previously to improve the heat resistance of silicones proved to be ineffective in lowering set.

RECOMMENDATIONS

It is recommended that a combination of additives, one which improves heat resistance and one which lowers set, be incorporated in silicones required to meet both maximum heat stability and low set requirements.

It is recommended that a study be made to develop a test method and procedure for determining the ability of an elastomeric vulcanizate which has been compressed at room temperature and then subjected to high temperature, to recover from deformation when removed from the compression set device and measured while still at high temperature.

COMPRESSION SET OF ELASTOMERS AT ELEVATED TEMPERATURES

CONTENTS

COMPRESSION SET OF ELASTOMERS AT ELEVATED TEMPERATURES

OBJECT

The objects of this investigation were: (1) to determine the compression set at temperatures up to 500°F of the most thermally stable elastomeric vulcanizates, and (2) to improve the compression set of these vulcanizates.

INTRODUCTION

This Arsenal has previously reported[1,2,3] data obtained on the high temperature capabilities and limitations of many types of elastomers, both after aging and when properties were measured at high temperatures. These data dealt with the effects of high temperatures on tensile, modulus, elongation, strain, hardness and percent weight loss, all of which are important. However, many rubbers are being used as gaskets or sealants where elastic recovery is an important factor. Data on compression set would be helpful in selecting vulcanizates for such applications.

During the past year, a study has been made to determine the set of heat resistant vulcanizates after they have been subjected, under compression, to temperatures up to 500°F. Attempts were also made to improve these properties. It is the purpose of this report to present the results obtained.

PROCEDURE

All compression set tests were performed using Method B (constant deflection method) of ASTM D395-55. Standard test specimens, 1/2" thick and 1.129" in diameter, were molded from compounds whose formulations are given in Table I. In order to provide equivalent states of cure for both pads and buttons, all set specimens were press cured one and one-half times longer than the press cure times given in the table for .075" thick test pads.

In some instances, various additives were used in the base formulations in attempts to improve set. This is discussed in detail in the results section of the report.

Set tests were carried out at 212°, 250°, 300°, 350°, 400°, 450° and 500° F. for periods as long as twenty-eight days. Tests were discontinued when a set value of 90 percent was reached, since it would be impractical to use a rubber having a set of 90 percent or higher.

TABLE I

COMPOUND FORMULATIONS

COMPOUNDING INGREDIENTS	A1E	S77C	N87C	I38	I38D	I40	I40C3	I48	I48D
Pale Crepe	100								
76.5/23.5 Butadiene/styrene (carbon black masterbatched)		150							
Butadiene/acrylonitrile (low acrylonitrile)			100						
Chlorinated isobutylene/isoprene				100				100	
Brominated isobutylene/isoprene					100	10	10		100
Isobutylene/isoprene (2.1 - 2.5 mole % unsaturation)						100	100		
Stearic acid	1	2	1	1	1	1	1	1	1
Zinc oxide	5	3	5	3	3	5	5	5	5
Phenyl beta naphthylamine	1	1		1	1				
Tetramethyl thiuram disulfide	3			1	1				
Elementary tellurium	0.5								
MT Carbon Black	25								
FT Carbon Black	25								
Dipentamethylene thiuram tetrasulfide		1	1.5						
2-mercaptobenzothiazole		1	1						
MAF Carbon Black			50			60	60		
Polymerized trimethyl dihydroquinoline			1						
Magnesium oxide				2	2				
HAF Carbon Black				60	60			50	50
Light processing oil				5	5				
Phenol formaldehyde resin				3	3	12.5	12.5		
Benzothiazyl disulfide				2	2				
Zinc diethyldithiocarbamate								1.5	1.5
	Press cure 30 min. @307°F	Press cure 30 min. @307°F	Press cure 30 min. @307°F	Press cure 30 min. @307°F	Press cure 30 min. @307°F	Press cure 30 min. @320°F	Press cure 60 min. @320°F	Press cure 45 min. @307°F	Press cure 45 min. @307°F

For trade names of compounding ingredients, see Code Sheet at end of report.

TABLE I (Cont.)

COMPOUNDING INGREDIENTS	Z83	Z98	Z98T	Z56C3	Z56C3T	Z81	Z81F	Z75DC	Z85	Z123
Vinylidene fluoride/hexafluoropropylene	100									
Dimethyl polysiloxane with vinyl groups attached - contains 20% reinforcing filler		100	100							100
Methyl vinyl silicone				100	100	100	100	100	100	
High strength silicone										
Fluorinated silicone										
Nitrile silicone										
Dimethyl silicone										
MT Carbon Black	20									
Magnesium oxide	15									
N,N'-Dicinnamylidene-1,6-hexanediamine	3									
Precipitated silica		8	8				10		55	40
Ground quartz		23	23							
50% Dichlorobenzoyl peroxide with silicone fluid		1.6	1.6	1.3	1.3	1.3	1.3		2.4	
50% Benzoyl peroxide with silicone fluid			2		2			0.8		0.8
Ferric oxide										
Tertiary butyl peroxide										
	Press cure 30 min. @307°F Step cure in air oven to 400°F Postcure 24 hrs. @400°F	Press cure 5 min. @240°F Postcure 8 hrs. @480°F	Press cure 5 min. @240°F Postcure 8 hrs. @480°F	Press cure 10 min. @275°F Postcure 8 hrs. @375°F	Press cure 10 min. @275°F Postcure 8 hrs. @375°F	Press cure 5 min. @240°F Postcure 24 hrs. @300°F	Press cure 5 min. @240°F Postcure 24 hrs. @300°F	Press cure 20 min. @340°F Postcure 24 hrs. @350°F	Press cure 10 min. @240°F Postcure 24 hrs. @480°F	Press cure 20 min. @340°F Postcure 24 hrs. @480°F

RESULTS

The first phase of this investigation dealt with the determination of set on vulcanizates which had been found previously by this Arsenal to possess good heat resistance, namely, various silicones and isobutylene/isoprene vulcanizates (including the brominated and chlorinated copolymers) and a vinylidene fluoride/hexafluoropropylene vulcanizate. NR, SBR and NBR elastomers were compounded for good aging resistance and used as control vulcanizates. Duplicate test results agreed within one or two percent in most cases and never varied by more than four percent. The results given in Table II reveal the following:

1. In some cases there is little relationship between the heat resistance of a vulcanizate (as measured by retention of tensile, modulus, elongation and strain) and its set. For example, vulcanizates which employ a phenol formaldehyde resin - tetramethyl thiuram disulfide - benzothiazyl disulfide curing system (I38 and I38D) have excellent heat resistance at elevated temperatures in comparison with other butyl vulcanizates[2], but have very high set at temperatures of only 212° and 250°F. On the other hand, vulcanizates prepared from compounds employing a zinc diethyldithiocarbamate curing system (I48 and I48D) have heat resistance almost identical to those employing the resin cure, but have set values that are much superior (lower). The set of the chlorinated vulcanizate (I48) is very good, being lower than some of the silicones.

2. Although cure time does not make a significant difference in the heat resistance of isobutylene/isoprene elastomers (based on percent change in tensile, modulus, elongation and strain) it may have a very pronounced effect on set. Vulcanizates of compound I40C3 were cured twice as long as those of compound I40. The heat resistance of these compounds are very similar as shown in Table III. The set at temperatures of 300°F and above, however, is much better for I40C3 than for I40. The cure time for I40 is considered to be optimum[4]. It appears from these data, however, that the cure time considered to be optimum for other properties may not give the lowest compression set.

3. The silicones did not have as good recovery at the higher temperatures as might be expected from their excellent thermal stability. This is especially true of the high strength silicone which had reached 100% set after 8 hours at 450°F.

TABLE II

COMPRESSION SET (PERCENT) OF VARIOUS VULCANIZATES AT HIGH TEMPERATURES

RIA CPD. NO.	ELASTOMER	22 HR. 212F	70 HR. 212F	7 DAYS 212F	14 DAYS 212F	28 DAYS 212F	22 HR. 250F	70 HR. 250F	7 DAYS 250F	14 DAYS 250F	28 DAYS 250F	22 HR. 300F	70 HR. 300F	7 DAYS 300F	14 DAYS 300F	28 DAYS 300F
A1E	Pale Crepe	26	31	41	47	54	38	43	48	54	64	51	73	75	86 split edges	-
S77C	Butadiene/styrene	28	36	47	51	59	46	46	52	59	71	61	71	95	-	-
N87C	Butadiene/acrylonitrile	15	17	25	28	36	23	25	28	40	57	38	52	87	94	-
I38	Chlorinated Isobutylene/ isoprene	50	82	88	88	90	78	81	88	85	89	-	-	-	-	-
I38D	Brominated Isobutylene/ isoprene	44	77	83	87	86	71	82	86	90	95	-	-	-	-	-
I40	Isobutylene/isoprene	46	48	63	66	68	55	61	68	70	77	70	77	78	93	-
I40C3	Isobutylene/isoprene	20	36	55	61	64	47	62	65	72	73	66	70	75	79	80
I48	Chlorinated Isobutylene/ isoprene	5	10	13	17	23	10	17	25	32	44	25	41	57	67	77
I48D	Brominated Isobutylene/ isoprene	20	23	32	36	48	24	38	49	59	70	51	65	79	88	93
Z98	Methyl vinyl silicone	14	29	37	39	46	19	33	41	50	61	29	48	63	82	89
Z98T	Methyl vinyl silicone	14	30	36	40	41	19	30	38	46	56	28	46	60	74	85
Z56C3	High strength silicone	14	32	43	45	55	28	38	44	53	59	44	63	65	82	82
Z56C3T	High strength silicone	15	35	48	48	56	34	43	52	57	59	45	63	65	83	83
Z81	Fluoro silicone	4	9	14	15	19	6	8	12	17	27	9	13	34	69	79
Z75DC	Nitrile silicone	-	34	44	51	56	-	45	50	58	-	-	-	-	-	-
Z83	Vinylidene fluoride/ hexafluoropropylene	30	37	43	44	51	26	39	43	52	59	30	41	50	52	60

TABLE II (Cont.)

RIA CPD. NO.	ELASTOMER	22 HR. 350F	70 HR. 350F	7 DAYS 350F	14 DAYS 350F	28 DAYS 350F	8 HR. 400F	16 HR. 400F	22 HR. 400F	70 HR. 400F	7 DAYS 400F	14 DAYS 400F	8 HR. 450F	16 HR. 450F	22 HR. 450F	70 HR. 450F	8 HR. 500F	16 HR. 500F
A1E	Pale Crepe	75	97	-	-	-	92	-	-	-	-	-	-	-	-	-	-	-
S77C	Butadiene/styrene	80	112	-	-	-	94	-	-	-	-	-	-	-	-	-	-	-
N87C	Butadiene/acrylonitrile	72	99	-	-	-	83	94	-	-	-	-	-	-	-	-	-	-
I40	Isobutylene/isoprene	87	94	-	-	-	89	93	-	-	-	-	-	-	-	-	-	-
I40C3	Isobutylene/isoprene	73	77	81	86	89	72	76	76	80	85	92	82	83	86	92	-	-
I48	Chlorinated Isobutylene/isoprene	52	71	82	88	98	64	73	79	89	95	-	88	100	-	-	-	-
I48D	Brominated Isobutylene/isoprene	76	99	-	-	-	84	96	-	-	-	-	111	-	-	-	-	-
Z98	Methyl vinyl silicone	49	68	86	92	-	34	62	70	93	-	-	88	106	-	-	122	-
Z98T	Methyl vinyl silicone	43	73	86	92	-	33	63	67	95	-	-	81	103	-	-	119	-
Z56C3	High strength silicone	70	90	-	-	-	83	98	-	-	-	-	105	-	-	-	-	-
Z56C3T	High strength silicone	72	91	-	-	-	86	98	-	-	-	-	100	-	-	-	-	-
Z81	Fluoro silicone	24	51	67	79	95	31	45	54	90	-	-	57	86	100	-	109	-
Z83	Vinylidene fluoride/hexafluoropropylene	38	55	61	73	75	33	46	55	72	83	92	52	73	75	94	84	100

TABLE III

PERCENT CHANGE IN PHYSICAL PROPERTIES OF ISOBUTYLENE/ISOPRENE VULCANIZATES AFTER AIR OVEN EXPOSURE

	PHYSICAL PROPERTIES	ORIGINAL	8 HR. @212F	8 HR. @250F	8 HR. @300F	8 HR. @350F	8 HR. @400F	8 HR. @450F	8 HR. @500F
I40	Tensile	1690 psi	+4	+4	+5	-11	-20	-41	-88
	Elongation	580%	-5	-19	-26	-38	-43	-36	+17
	Strain (400 psi load for 60 sec)	174	-8	-20	-26	-26	-24	+7	Broke
I40C3	Tensile	1710 psi	+9	-2	-3	-12	-18	-47	Specimens had no strength
	Elongation	510%	-14	-22	-33	-35	-43	-41	
	Strain (400 psi load for 60 sec)	133	-8	-13	-19	-22	-20	+8	

4. The addition of ferric oxide to methyl vinyl and high strength silicones has little or no effect on the set. It has long been recognized[5,6,7,8] that the addition of ferric oxide improved the thermal stability.

5. A vinylidene fluoride/hexafluoropropylene vulcanizate (Z83) was the only one which had a value below 90% after 8 hours at 500°F. This rubber also had the lowest set when exposed 14 days at 300°F, 7 days at 350°F, 70 hours at 400°F or 8 hours at 450°F.

Previous work[3] revealed that several additives had improved the thermal stability of a methyl vinyl silicone. The results presented in Table II, however, show that ferric oxide, one of the most effective additives for improving the heat resistance of a methyl vinyl silicone (Z98), does not improve the set of this vulcanizate. It was revealed in the literature that mercuric oxide[5] and cadmium oxide[6,10] improve the set of silicones. However, it was found by this Arsenal[3] that neither of these chemicals improved the resistance to high temperatures of a methyl vinyl silicone. It was therefore decided to re-evaluate all those additives which did not degrade the original physical properties of the Z98 silicone. Some additional additives were also used, a complete list being furnished in the Appendix. These additives were evaluated at a concentration of two parts unless otherwise indicated. Seven (barium oxide, cadmium oxide, calcium oxide, calcium hydroxide, magnesium oxide, praeseodymium oxide and strontium oxide) were found to lower the set of a methyl vinyl silicone. These data are given in Table IV.

It was found that these additives were not as effective, however, in this vulcanizate (Z98) when the buttons were postcured 24 hours at 480°F instead of 8 hours at 480°F. The 24 hour postcure reduces the set of the control as shown below:

	Exposed 7 days @300°F	Exposed 70 hr. @350°F	Exposed 22 hr. @400°F	Exposed 8 hr. @450°F
Postcured 8 hr. @480°F	63	68	70	88
Postcured 24 hr. @480°F	35	48	45	46

Cadmium oxide was the only additive which significantly lowered the set after a postcure of 24 hours at 480°F. This is shown in Table V where samples based on the two postcures have been exposed at 300°F. The manufacturer of this silicone

TABLE IV

IMPROVEMENT IN SET OF A METHYL VINYL SILICONE BY VARIOUS ADDITIVES

Additive	Parts/ 100 rhc	7 Days 212F	7 Days 300F	70 Hour 350F	22 Hour 400F	8 Hour 450F	8 Hour 500F
None - Control	-	39	63	68	70	88	122
Barium oxide	2	30	52	45	39	37	73
Cadmium oxide	2	19	40	50	41	41	113
Calcium hydroxide	2	21	43	44	34	40	88
Calcium oxide	2	24	44	48	45	41	94
Magnesium oxide	2	21	40	35	34	32	73
Praeseodymium oxide	2	29	41	38	41	39	84
Strontium oxide	2	19	51	44	39	35	75

TABLE V

EFFECT OF POSTCURE TIME ON EFFECTIVENESS OF ADDITIVES FOR LOWERING SET IN METHYL VINYL SILICONE

	Exposed 22 hrs. @300F		Exposed 70 hrs. @300F	
Additive	Postcured 8 hours @480°F	Postcured 24 hours @480°F	Postcured 8 hours @480°F	Postcured 24 hours @480°F
None - Control	33	16	50	31
Barium oxide	17	14	31	30
Calcium hydroxide	17	14	31	29
Calcium oxide	19	20	29	30
Cadmium oxide	8	6	22	10
Magnesium oxide	22	14	40	26
Praeseodymium oxide	23	15	38	31
Strontium oxide	19	15	31	28

recommends[8] oven postcures of 4 to 24 hours at 480°F to develop an optimum balance of properties. The postcure time is varied from 4 to 24 hours to obtain different combinations of properties to meet specific specification or job requirements. The postcure used most frequently in testing the Z98 vulcanizate was 8 hours at 480°F since this was the time recommended[9]. The 8 hour postcure gives a 50±5 Shore A hardness while the 24 hour postcure gives 60±5. It can be seen in Table V that the set at 300°F of the controls postcured 24 hours at 480°F are lower than those postcured 8 hours at 480°F. The use of additives in the vulcanizates postcured 8 hours at 480°F lowered the set in many cases to the same range as that of those postcured 24 hours at 480°F. Also, the good high temperature resistance was not adversely affected at temperatures of 600°F and 700°F by the longer postcure time (24 hours vs. 8 hours). The Z98T compound is the most heat resistant silicone found by this Arsenal.

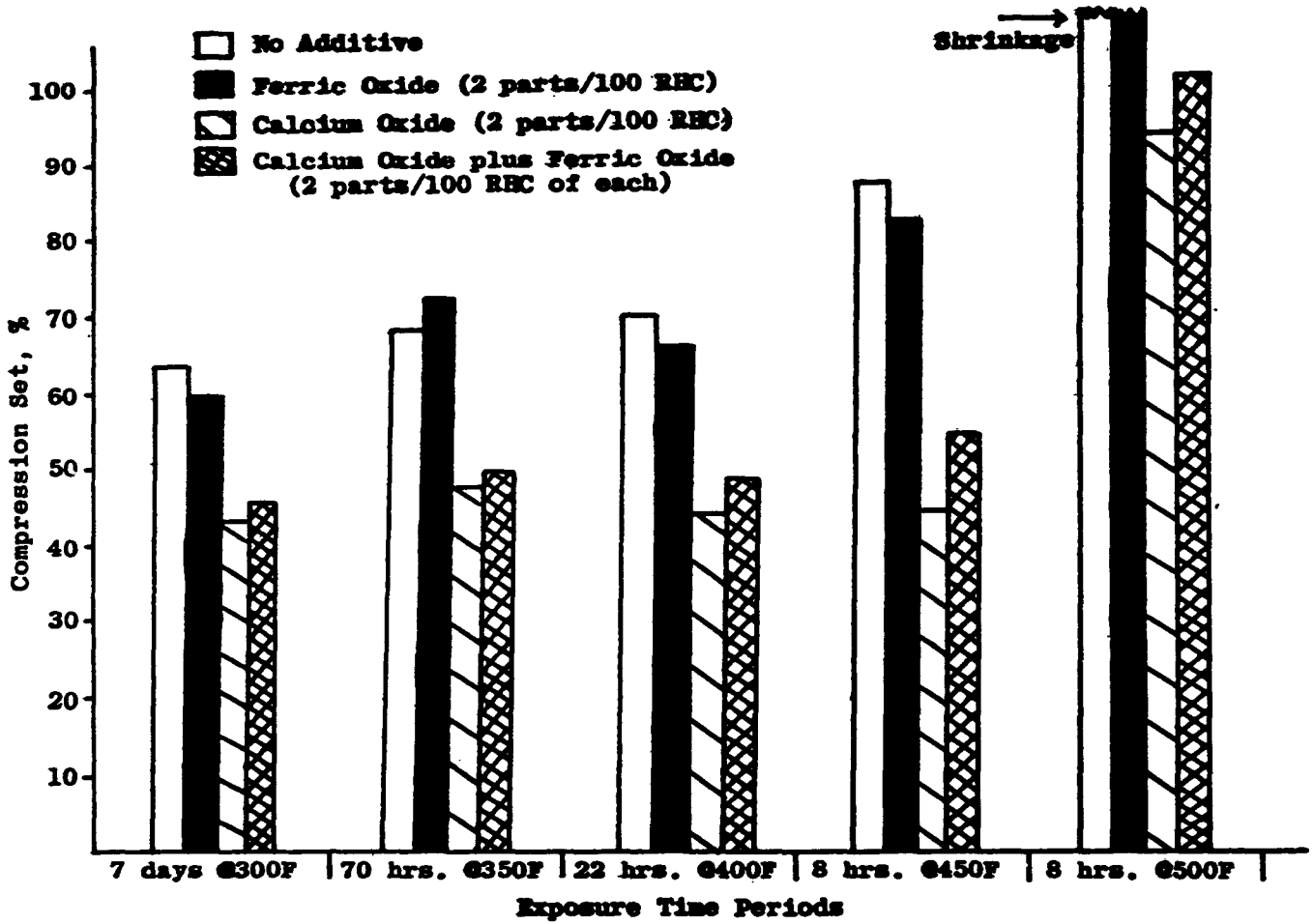
None of the additives which improved the thermal stability of the Z98 were effective in improving the set. Likewise, none of the seven additives which lowered the set of vulcanizates postcured 8 hours at 480°F improved the heat resistance. Concentrations of 5 and 10 parts of the additives did not improve the set over those containing only two parts. However, those containing two parts had lower set in most cases than those containing one.

Various combinations of additives found to be effective in improving heat resistance and in lowering set were evaluated in a methyl vinyl silicone. It was found that a vulcanizate containing a combination of two parts ferric oxide and two parts calcium oxide had both improved heat resistance and improved set. The improvement in set is shown graphically in Figure 1, and the improvement in heat resistance is shown in Table VI.

A study was also made to determine whether those additives found to be effective in lowering the set of a methyl vinyl silicone postcured 8 hours at 480°F (Z98) would be as effective in improving the set of a high strength (Z56C3), fluoro (Z81F), and dimethyl (Z85) silicone and another methyl vinyl silicone compounded for low set (Z123). The results of this evaluation are given in Table VII and reveal the following:

1. Some of the additives were not as effective in lowering the set of the high strength, fluoro and dimethyl silicones as they were in lowering that of the methyl vinyl silicone. Cadmium oxide, for example, was the only additive which significantly improved the set of the dimethyl silicone.

FIGURE 1



COMPRESSION SET OF SILICONE VULCANIZATES CONTAINING CALCIUM OXIDE AND/OR FERRIC OXIDE

TABLE VI

HEAT RESISTANCE OF SILICONE VULCANIZATES CONTAINING CALCIUM OXIDE AND/OR FERRIC OXIDE

NO ADDITIVE - CONTROL

PHYSICAL PROPERTIES	ORIGINAL	AGED 70 HRS. @600°F	AGED 7 DAYS @600°F	AGED 2 HRS. @700°F	TESTED @300°F
T	840	500	Brittle	Brittle	580
100% M	120	-	"	"	200
200% M	410	-	"	"	490
300% M	680	-	"	"	-
% E	420	50	"	"	230
H	50	86	"	"	-

FERRIC OXIDE (2 PARTS)

PHYSICAL PROPERTIES	ORIGINAL	AGED 70 HRS. @600°F	AGED 7 DAYS @600°F	AGED 2 HRS. @700°F	TESTED @300°F
T	780	400	450	220	570
100% M	130	-	-	-	220
200% M	450	-	-	-	480
300% M	690	-	-	-	-
% E	360	90	80	50	230
H	51	70	75	71	-

CALCIUM OXIDE (2 PARTS)

PHYSICAL PROPERTIES	ORIGINAL	AGED 70 HRS. @600°F	AGED 7 DAYS @600°F	AGED 2 HRS. @700°F	TESTED @300°F
T	610	520	Brittle	Brittle	460
100% M	130	-	"	"	170
200% M	360	-	"	"	370
300% M	560	-	"	"	-
% E	350	50	"	"	230
H	48	85	"	"	-

CALCIUM OXIDE PLUS FERRIC OXIDE (2 PARTS)

PHYSICAL PROPERTIES	ORIGINAL	AGED 70 HRS. @600°F	AGED 7 DAYS @600°F	AGED 2 HRS. @700°F	TESTED @300°F
T	840	600	570	350	600
100% M	200	-	-	-	260
200% M	540	-	-	-	580
300% M	710	-	-	-	-
% E	320	100	70	50	210
H	55	77	85	78	

Note: T = Tensile, psi
M = Modulus, psi
E = Ultimate Elongation, %
H = Hardness, Shore A

TABLE VII

EFFECTIVENESS OF ADDITIVES IN IMPROVING SET OF VARIOUS SILICONES

High Strength Silicone (Z56C3)

Additive	Parts/ 100 rhc	70 Hrs @250°F	70 Hrs @300°F	22 Hrs @350°F	8 Hrs @400°F
None - Control	-	38	63	70	83
Barium oxide	2	39	52	50	52
Cadmium oxide	2	31	54	58	63
Calcium hydroxide	2	28	43	50	55
Calcium oxide	2	33	48	59	59
Magnesium oxide	2	32	57	54	56
Praeseodymium oxide	2	35	49	52	49
Strontium oxide	2	21	42	47	50

Fluoro Silicone (Z81F)

Additive	Parts/ 100 rhc	7 Days @300°F	70 Hrs @350°F	22 Hrs @400°F	16 Hrs @450°F
None - Control	-	26	25	39	92
Barium oxide	2	13	14	18	47
Cadmium oxide	2	21	22	38	79
Calcium hydroxide	2	15	10	17	53
Calcium oxide	2	17	19	23	55
Magnesium oxide	2	26	21	26	41
Praeseodymium oxide	2	26	24	21	51
Strontium oxide	2	14	10	12	68

Dimethyl Silicone (Z85)

Additive	Parts/ 100 rhc	70 Hrs @212°F	70 Hrs @250°F	70 Hrs @300°F	8 Hrs @350°F
None - Control	-	69	78	85	72
Barium oxide	2		Not Compatible		
Cadmium oxide	2	19	27	48	18
Calcium hydroxide	2	69	76	86	64
Calcium oxide	2	62	65	74	57
Magnesium oxide	2		Not Compatible		
Praeseodymium oxide	2	66	76	79	68
Strontium oxide	2	67	76	84	72

TABLE VII (Cont.)

Methyl Vinyl Silicone Vulcanizate (Z123)

Additive	7 Days @250°F	70 Hrs @300°F	22 Hrs @350°F	22 Hrs @400°F	8 Hrs @500°F
None - Control	20	17	16	22	43
Barium oxide	17	19	17	21	35
Calcium hydroxide	17	17	15	18	37
Calcium oxide	17	15	16	19	34
Cadmium oxide	17	14	13	21	39
Magnesium oxide	18	17	15	19	38
Strontium oxide	19	16	15	18	35

2. There is no one additive which improves the set of all four types of silicones studied. However, the set of compounds Z56C3, Z81F, and Z85 could be improved by one or more additives.

3. Compound Z123 is a methyl vinyl silicone especially compounded for low set, and it is to be noticed that its set is very low at high temperatures. None of the additives significantly improved the set of this vulcanizate. However, even when ferric oxide is added to this compound it does not have as good heat resistance as the other methyl vinyl silicone studied, Z98T. Specimens of Z123 containing 2 parts ferric oxide are brittle after exposure for 7 days at 600°F or two hours at 700°F in an air oven whereas Z98T specimens are still flexible after similar exposure.

Calcium oxide and cadmium oxide were evaluated in SBR (S77C), NBR (N87C), NR (AIE), IIR (I40C3), chlorobutyl (I48), bromobutyl (I48D) and vinylidene fluoride/hexafluoropropylene (Z83) vulcanizates to determine if the set of these vulcanizates could be lowered. The only vulcanizate which showed significant improvement in set without having its original physical properties affected was the NBR (N87C) containing two parts calcium oxide. The improvement in set is shown in Table VIII. The addition of two parts cadmium oxide to the SBR and NBR vulcanizates produced lower set (Table X), but the original physical properties were altered as shown in Table IX.

TABLE VIII

IMPROVEMENT IN THE SET OF NBR BY CALCIUM OXIDE

Additive	Parts/ 100 rhc	70 Hrs @212°F	22 Hrs @250°F	22 Hrs @300°F	22 Hrs @350°F
None - Control	-	17	23	38	72
Calcium oxide	2	15	14	27	56

TABLE IX

PHYSICAL PROPERTIES OF SBR AND NBR CONTAINING CADMIUM OXIDE

Physical Property	SBR		NBR	
	No Additive (Control)	Cadmium Oxide	No Additive (Control)	Cadmium Oxide
Tensile, psi	3150	2680	2510	2610
100% Modulus, psi	240	430	300	740
200% Modulus, psi	510	1100	880	2110
300% Modulus, psi	1040	2070	1790	-
Ultimate Elongation, %	680	370	400	250
Hardness, Shore A	65	66	63	70

TABLE X

SET OF SBR AND NBR CONTAINING CADMIUM OXIDE

	Additive	Parts/ 100 rhc	70 Hrs @212°F	22 Hrs @250°F	22 Hrs @300°F	22 Hrs @350°F
SBR	None - Control	-	36	46	61	80
	Cadmium oxide	2	22	20	31	54
NBR	None - Control	-	17	23	38	72
	Cadmium oxide	2	7	6	17	37

The NR compound containing cadmium oxide did not cure. The addition of calcium oxide to the NR had no effect on either the physical properties or the set.

Both the calcium and cadmium oxides retarded the cure of the butyl vulcanizates (I48, I48D, and I40C3). This retardation of cure was very pronounced when the calcium oxide was used. The set of the vulcanizates containing the calcium and cadmium oxides were generally poorer than the control compound containing no additive.

The addition of the calcium and cadmium oxides to the vinylidene fluoride/hexafluoropropylene vulcanizates had no effect on either the original physical properties or set.

DISCUSSION

It was found that calcium, cadmium, praeseodymium, barium, magnesium and strontium oxides improved the set of some silicone vulcanizates at elevated temperatures. It is interesting to note that all of the metals of the effective oxides, except praeseodymium, fall in group II of the periodic listing of the elements. Mercury, the oxide of which is often quoted in the literature as improving the set of silicones, also falls in the group II classification (this additive when evaluated in the Z98 formulation, however, caused the specimens to become porous and puffy during postcure, and set could not be determine).

Many of the high temperature rubbers available today are used as compression gaskets at elevated temperatures. If the gaskets are cooled to ambient temperatures before being relieved from the compression deformation, their ability to recover from the deformation can be measured by the ASTM D395 procedure. If, however, the compression is released with the gasket at the high exposure temperature, the ASTM procedure becomes inadequate. It is the opinion of this Arsenal that a test method should be developed for determining the set of vulcanizates which are: (1) tested at high temperature, (2) allowed to recover from deformation at high temperature, and (3) measured at high temperature. This should be an additional compression set test and not a replacement for the currently used ASTM method since it is felt that a knowledge of the compression set of vulcanizates which have been tested at high temperatures and then allowed to recover at room temperature is also very useful for many applications.

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APPENDIX

Additives Evaluated to Improve the Compression Set Properties of a Methyl Vinyl Silicone Vulcanizate

Antimony trioxide
Barium oxide
Barium zirconate
Beryllium oxide
Cadmium oxide
Calcium carbonate
Calcium hydroxide
Calcium oxide
Cerium oxide
Chromium oxide
Cobalt oxide
Copper oxide
Erbium oxide
Europium oxide
Ferric fluoride*
Ferric formate*
Ferric octoate* (1)
Ferric oxide
Ferric pyrophosphate*
Ferric sulfide
Gadolinium oxide
Gallium oxide
Hafnium oxide
Holmium oxide
Iron phosphate (ins.)
Iron silicate*
Lanthanum oxide
Magnesium oxide
Manganese dioxide* (1)
Mercury oxide*
Molybdenum oxide
Neodymium oxide
Nickel oxide
P-33 Carbon black* (1)
Platinum oxide*
Praeseodymium oxide
Scandium oxide
Silver oxide
Stannic oxide
Strontium oxide
Tantalum pentoxide
Terbium oxide
Thorium oxide
Thulium oxide
Titanium oxide
Ytterbium oxide
Zinc oxide
Zirconium oxide
Zirconium silicate
2,5 ditertiary butyl-p-benzoquinone*

*Compression set buttons become porous and puffy during postcure - set values were, therefore, not determined.

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76.5/23.5 Butadiene/ styrene (carbon black masterbatched)	SBR 1600	Goodyear Tire & Rubber Co.
Butadiene/acrylonitrile (low acrylonitrile)	Paracril 18-80	Naugatuck Chem. Division
Chlorinated Isobutylene/ isoprene	HT-1066	Enjay Company, Inc.
Brominated Isobutylene/ isoprene	Hycar 2202	B.F. Goodrich Chem. Company
Isobutylene/isoprene (2.1-2.5 mole % unsaturation)	325 Butyl	Enjay Company, Inc.
Vinylidene fluoride/ hexafluoropropylene	Viton B	E.I. duPont de Nemours & Co.
Dimethyl polysiloxane with vinyl groups attached - contains 20% reinforcing filler	Silastic 432 Base	Dow Corning Corp.
Methyl vinyl silicone	W-96	Union Carbide Corp.
High strength silicone	SE 555U	General Electric
Fluorinated silicone	LS 422 Base	Dow Corning Corp.
Nitrile silicone	Y-3198	Union Carbide Corp.
Phenyl-beta-naphthylamine	Neozone D	E.I. duPont de Nemours & Co.
Tetramethyl thiuram disulfide	Methyl Tuads	R.T. Vanderbilt Co.
Elementary tellurium	Telloy	R.T. Vanderbilt Co.

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Dipentamethylene thiuram tetrasulfide	Tetrone A	E.I. duPont de Nemours & Co.
2-mercaptobenzothiazole	Captax	R.T. Vanderbilt Co.
MAF Carbon black	Philblack A	Phillips Petroleum Co.
Polymerized trimethyl dihydroquinoline	Agerite Resin D	R.T. Vanderbilt Co.
HAF Carbon black	Philblack O	Phillips Petroleum Co.
Light Processing Oil	Circo Light Processing Oil	Sun Oil Company
Phenol formaldehyde resin	Amberol ST-137	Rohm & Haas Co.
Benzothiazyl disulfide	Altax	R.T. Vanderbilt Co.
Zinc diethyldithio-carbamate	Ethyl Zimate	R.T. Vanderbilt Co.
N,N'-Dicinnamylidene-1,6-hexanediamine	Diak #3	E.I. duPont de Nemours & Co.
Precipitated silica	Hi Sil X303	Columbia-Southern Chemical Corp.
Ground quartz	Neo Novacite	Malvern Minerals Co.
50% Dichlorobenzoyl peroxide with silicone fluid	Cadox T.S. Paste	Cadet Chemical Corp.
50% Benzoyl peroxide with silicone fluid	Cadox S.G. Paste	Cadet Chemical Corp.
Dimethyl silicone	SE-30	General Electric

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RIA Lab. Rep. 63-798, 14 Mar 63, 24 p. incl. illus. tables, (DA Project No. 1-H-0-24401-A-111, AMC Code No. 5026.11.843) Unclassified report.

Compression set tests (constant deflection method of ASTM D395-55) were carried out on heat resistant rubber vulcanizates for periods as long as 28 days at temperatures up to 500°F. It was found that some silicone rubbers did not have set values at elevated temperatures as low as might be expected from their excellent resistance to heat aging. Cure time was found to have a significant effect on the set of isobutylene/isoprene vulcanizates. Increased cure time resulted in lower set even though the original cure time may have been optimum for other properties.

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Certain metal oxide additives significantly lowered the set of some silicones. No one additive was found, however, which lowered the set of all four types of silicones; namely, dimethyl, methyl vinyl, fluoro and high strength. Additives which had been found previously to improve the heat resistance of silicones proved to be ineffective in lowering set.

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