

**DEVELOPMENT OF A RUBBER FOR SERVICE IN
CONTACT WITH EXPERIMENTAL HYDRAULIC
FLUIDS AT 400°F**

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FOREWORD

This report was prepared by the Organic Materials Branch and was initiated under Project No. 7340, Rubber Plastic and Composite Materials, Task No. 73405, Compounding of Elastomers, formerly RDO No. 617-12, Compounding of Elastomers, and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. F. G. Kitts acting as project engineer.

Many of the materials tested were not developed or intended by the manufacturer for the conditions to which they have been subjected. Any failure or poor performance of a material is therefore not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

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ABSTRACT

The operation of hydraulic systems of piloted supersonic aircraft at temperatures in the neighborhood of 400°F will necessitate the replacement of standard AN seals and hose with a more heat and fluid resistant compound. Earlier work had proved Buna N (Butadiene-Acrylonitrile Copolymers) unsatisfactory over the temperature range -65° to 400°F in the silicate ester type fluids so Neoprene WRT was chosen as the best overall compromise of original and aged physical properties.

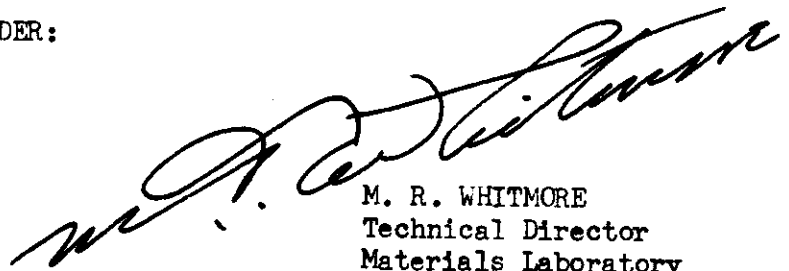
A compound of Neoprene WRT was developed which was marginally satisfactory after aging 168 hours in MLO 8200 at 400°F in the absence of air. If air were not at least partially excluded the rubber would reach an unsatisfactory condition in the less than 70 hours. It was found that a blend of 85 parts of MLO 8200 and 15 parts of di(2 ethyl hexyl) sebacate with anti-oxidant added to bring the concentration in the blend up to the original concentration in MLO 8200 gave the best balance of aged properties with Neoprene WRT with and without air above the fluid surface.

The compounds of Neoprene WRT are believed to be processable on industrial equipment such as mills, extruders, etc. "O" rings have been fabricated in the Materials Laboratory and are undergoing evaluation testing.

PUBLICATION REVIEW

This report has been reviewed and is approved.

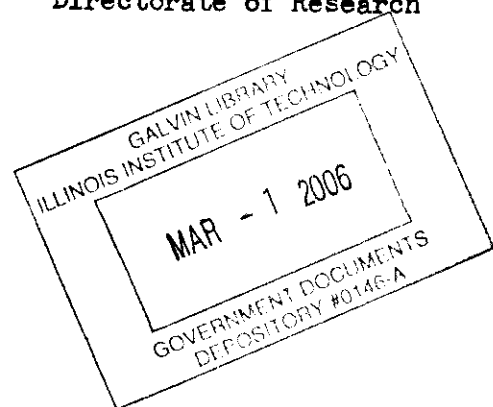
FOR THE COMMANDER:



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INTRODUCTION

The increased operating temperatures in the hydraulic systems of supersonic piloted aircraft coupled with the necessity of subjecting such aircraft to environmental extremes has made necessary the development of rubber seals, hose, gaskets, etc. which will function over the temperature range -65 to 400°F in contact with the hydraulic fluid. This is not to be confused with the requirement for a rubber to withstand temperatures in excess of 500°F for short times; the -65 to 400°F requirement is strictly a long service-time proposition up to 1000 hours if possible.

The development of a rubber for the high temperature hydraulic fluid was begun long before the fluid was fully developed. The first work, reported in Materials Laboratory Memorandum Report WCRTE-M5572, was done with an early silicate ester fluid MLO 5277 and showed Neoprene W to be the best elastomer for use with the fluid. Since then the final fluid MLO 8200 has been made available and Neoprene WRT with improved low temperature properties was placed on the market. The present approach is to develop a compound based on Neoprene WRT which will be compatible with MLO 8200, or some blend principally MLO 8200, over the required temperature range.

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SECTION I

TESTING TECHNIQUE

Since the purpose of this work was to develop a rubber compound to be used in various forms in contact with the hot fluid, it was decided that all aging tests should be made by total immersion of samples in fluid at the maximum temperature expected in the actual hydraulic system. The samples were dumb-bells as shown in Federal Specification ZZ-R-601a; immersion times and conditions were as indicated in Appendix II. The principal fluid was MLO 8200, a silicate ester base hydraulic fluid developed under Air Force contract by the California Research Corporation.

Each dumb-bell was placed in a 75ml test tube containing approximately 50ml of fluid; since all the samples weighed less than 2.5 grams there was always at least 20ml of fluid present per gram of rubber. Test tubes were placed upright in an aluminum rack and aged in a circulating air oven equipped with a full-time temperature recorder. In tests where a closed system is indicated a pyrex thimble was inserted in the mouth of the test tube forming a loose seal.

After removal from the oven, samples were allowed to cool to room temperature in the fluid, then removed and allowed to stand overnight in air. Physical properties were then determined in accordance with Federal Specification ZZ-R-601a. Volume change was determined immediately after cooling from test temperature. All hardness values reported are Shore "A" durometer. Brittle point values were obtained using an ASTM, solenoid driven, Scott machine.

SECTION II

MILLING PROCEDURE

The Neoprene WRT is banded easily on the mill at room temperature. A laboratory mill with 3 inch diameter rolls was used for all mixing. A movable guide allows the width of the sheet to be varied up to 6 inches depending on the size of the batch and the bank desired. Since no stearic acid is to be used in most cases, a 1/8" inch thick band should be maintained to avoid excessive breaking down and sticking. A few drops of the plasticizer may be added here if necessary. The zinc and magnesium oxides, and NA-22 are mixed, added, and dispersed well. Milling temperature is not critical; however, cold water should be used if there is danger of scorching. The two blacks should be stirred together and added next. It will probably be necessary to begin adding the plasticizer before all the black is in. As more of the plasticizer is added the temperature of the rolls will have to be lowered in order to maintain strength in the soft band. The band may be easily sheeted off a cool mill and should be laid on a surface to which it will not adhere.

Continents

SECTION III

COMPOUNDING INFORMATION

The recommended compound, 453-26C, resulting from this investigation was developed by considering five main constituents or groups of constituents.

First, in a compound of this type, the base polymer is the most important. Since here both -65°F flexibility and moderate oil resistance are required along with high temperature resistance, only the Neoprenes and Buna N's were considered. Since the Buna N's have been shown to exhibit severe surface cracking under conditions encountered here, only the Neoprenes were left. Neoprene WRT was chosen because of its superior low temperature properties.

For a Neoprene vulcanizate to have -65°F flexibility it must contain a plasticizer. Early work showed shrinkage of plasticized stocks to be a problem; the approach then should be a smaller amount of a more efficient plasticizer. Butyl oleate was chosen as the best common low temperature plasticizer for Neoprene WRT.

The filler loading of a heat resistant compound is also of prime importance. The two-black system used here was taken from the previous work cited in the Introduction; other loadings were tried, but none aged as well as this combination.

Many different combinations of metallic oxides and accelerators may be used to cure Neoprene. For a high temperature resistant compound a high concentration of zinc oxide is usually recommended. However, in this case compounds with low zinc oxide concentrations consistently showed higher retention of physical properties after aging in MLO 8200. It is not claimed that the curing system of the end compound -26C is the best obtainable; it was the best to date when rubber parts had to be supplied to allow fluid testing to proceed.

In earlier work not reported here, several common anti-oxidants were tested and none was found to exhibit any outstanding beneficial effects in the neighborhood of 400°F . This investigation shows that the use of common anti-oxidants consistently results in inferior retained physical properties after aging in MLO 8200 at 400°F .

SECTION IV

DISCUSSION

It was felt early in the fluid development program that silicate esters would not be compatible with standard AN packings at proposed temperatures of operation. Some work was done about two years ago on an early silicate ester fluid. When the final fluid MLO 8200 became available the best compound of

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the previous investigation was reproduced, designated 453-19D and tested first in MLO 8200. This combination left much to be desired; the rubber hardened, shrank and lost most of its elongation after only 70 hours at 400°F in the fluid. Either the rubber or the fluid had to be changed; so additions of diesters were made to the fluid and showed a definite improvement in the physical properties of the aged rubber samples. No effort was made to determine which diester was best; one known as a good rubber plasticizer was arbitrarily chosen.

Keeping in mind the effect of fluid additives, work was begun to develop a better rubber for straight MLO 8200. As a new approach amine-cured Neoprenes were tried since amine cures in other kinds of rubber gave heat-resistant vulcanizates. These compounds, shown in Table I, could hardly be processed without scorching; the curing agent was dissolved in the plasticizer, added after the plasticizer and absorbed in the black, but scorching was still evident. Dumb-bells of the material cracked upon elongation when determining only original physical properties so this approach was abandoned.

The next approach was the use of a more efficient low temperature plasticizer. Each compound was not checked individually for -65°F flexibility, but the class of compounds, containing 15 parts of butyl oleate, will have brittle points in the neighborhood of -65°F. If a particular compound does not make -65°F a small adjustment of plasticizer content will bring the low temperature properties to the desired level. Parco compound 363-70, submitted by Plastic and Rubber Products Company, Los Angeles, California, ages very well but does not have -65°F flexibility originally.

At first high zinc oxide concentrations were used in an attempt to gain high temperature resistance but compounds of this type became brittle and exhibited internal bubbling. When this was observed in original swell tests, no further testing was conducted. Compounds with low zinc oxide concentrations did not show bubbles and generally were more flexible after aging.

It was at about this point that a difference was noted in samples aged in open and partially closed containers. The samples in the absence of air exhibited more swell and better aged physical properties. This difference was considered significant so all compounds which had been tested in open test tubes were re-evaluated in the absence of air.

When a compound with usable aged physical properties had been developed, attention was again turned to the fluid. This usable compound 453-26C was tested in a series of MLO 8200/diester blends to determine the effect of diester concentration upon the rubber. It was discovered that about an 85/15 blend gave optimum aged properties. Low temperature properties, tensile, hardness, and elongation were retained without excessive swell.

Although, a great deal of work has been done on the high temperature fluid-seal combination, no concrete decision has been made to date as to what the final fluid will be. To give all the proposed fluids an equal chance, a proposed fluid specification MIL-F-8146, has been initiated. The rubber swell requirement of this specification has been established as 25±5% swell on either standard stock "L" or a standard unplasticized Neoprene WRT designated stock "R". Swell tests of stock "R" in MLO 8200 and various blends are shown in Appendix II, Table VI; the values for stock "L" are also shown for comparison.

Contracts
APPENDIX I

RECIPES AND ORIGINAL PHYSICAL PROPERTIES

TABLE I

COMMERCIAL AND AMINE VULCANIZED COMPOUNDS

	453- 19E	21A	21B	21G	LINEAR LFR-60X11	PARCO 363-70	"R"	"L"
NEOPRENE WRT	100	100	100	100				
SRF BLACK	40	40	40		A BUNA-N CPD. OF UNKNOWN COMPOSITION	A NEOPRENE CPD. OF UNKNOWN COMPOSITION		
MT BLACK	40	40	40					
STEARIC ACID	.5							
TRIETHYLENETETRAMINE	1.3	1.35	1.3					
TRIMENE BASE				1.5				
HAF BLACK				50				
TP-90B	20							
BUTYL OLEATE		15	15	15				
THERMOFLEX A			1.5					
NEOZONE A			1.5					

CURES 20' at 310°F

ORIGINAL PHYSICAL PROPERTIES

TENSILE PSI	1500	1000	850	690	1975	2065	-	-
ELONGATION %	280	92	175	250	150	350	-	-
HARDNESS SHORE A	66	72	52	50	73	69	-	-

TABLE II

COMPOUNDS CONTAINING ANTI-OXIDANTS

	453-21B	-21C	-19D	-19F	-26C-1	-21D	33C
NEOPRENE WRT	100	100		100	100	100	100
NEOPRENE W			100				
ZINC OXIDE	10	5	5	5	2.5	2.5	2
MAGNESIUM OXIDE	4	4	2	2	4	1	2
NA-22	1	1.5	1.5	1	1	.75	.4
SRF BLACK	40	40	40	40	40	40	60
MT BLACK	40	40	40	40	40	40	
THERMOFLEX A	1.5	1.5	1.5	1.5	1.5	1.5	1.5
NEOZONE A		1.5	1.5	1.5	1.5	1.5	1.5
BUTYL OLEATE	15	15		15	15	15	15
ARANOX	1.5						
STEARIC ACID			.5				
TP-90B			20				

CURES: 20' at 310°F

ORIGINAL PHYSICAL PROPERTIES

TENSILE PSI	1840	1970	2050	-	2000	1960	2040
ELONGATION %	240	255	275	-	237	280	350
HARDNESS SHORE A	61	65	62	-	67	61	60

TABLE III

COMPOUNDS CONTAINING NO ANTI-OXIDANTS

	453- 21F	26A	25A	25B	26B	26C	33B	33A	33D
NEOPRENE WRT	100	100	100	100	100	100	100	100	100
ZINC OXIDE	10	10	10	10	5	2.5	1	1	-
MAGNESIUM OXIDE	4	4	2	2	2	4	3	1	3
NA-22	1	1	1	1	1	1	1	1	-
SRF BLACK	40	40	40	40	40	40	40	40	40
MT BLACK	40	40	40	40	40	40	40	40	40
BUTYL OLEATE	15	15	-	15	15	15	15	15	15

CURES: 20' at 310°F

ORIGINAL PHYSICAL PROPERTIES

TENSILE PSI	1640	1700	2170	1540	1790	1720	1910	1915	1200
ELONGATION %	190	200	147	182	195	193	200	200	520
HARDNESS SHORE A	61	67	76	61	66	64	69	66	52

AGED PHYSICAL PROPERTIES

TABLE I

COMPOUND 453-19D 70 HOURS IN MLO 8200/DOS BLENDS AT 400°F IN AIR

Fluid	% Volume Change
MLO 8200	-2
95/5	+6
90/10	+8
85/15	+9

APPENDIX II

TABLE II

AMINE VULCANIZED COMPOUNDS 70 HOURS IN MLO 8200 AT 400°F IN AIR

COMPOUND	TENSILE	% ELONGATION	HARDNESS
453-19E	1230	33	90
453-21G	-	10	95

APPENDIX II

TABLE III

TESTS IN 90/10 MLO 8200/DOS BLENDS AT 400°F IN AIR

COMPOUND	TIME	TENSILE	% ELONGATION	HARDNESS	% VOL. CHANGE
453-21C	70	875	95	71	+2.5
-21D	70	740	70	74	+12.5
-25A	48	-	-	-	+16.0
-25B	48	-	-	-	+5.5
-26A	70	-	-	95	+4.0
-26B	70	3000	5	95	+7.0
-26C	70	1360	55	85	-2.0

TABLE IV

TESTS IN MLO 8200 AT 400°F

COMPOUND	TIME	SYSTEM	TENSILE	% ELONGATION	HARD	% VOLUME CHANGE
453-19D	64	OPEN	-	0	100	-3.
453-19F	70	OPEN	-	-	-	+8.
21C	70	OPEN	1060	88	76	-2.8
21D	70	OPEN	1145	62	77	+7.3
21E	70	OPEN	750	65	78	-1.4
21F	70	OPEN	1350	87	77	-
25A	48	OPEN	-	-	-	+1.2
25B	48	OPEN	-	-	-	-9.5
26A	70	OPEN	1600	85	86	-7.5
26B	70	OPEN	-	35	90	-9.0
26C	70	OPEN	1500	80	83	-6.7
21F	70	CLOSED	-	-	100	-
25B	70	CLOSED	-	-	100	-
26A	70	CLOSED	-	-	100	-
26B	70	CLOSED	-	-	100	-
PARCO-363-70*	70	CLOSED	1600	145	76	+9.7
LINEAR LFR-60	70	CLOSED	950	35	86	0.0
453-33A*	70	CLOSED	1600	47	85	0.9
-33B	70	CLOSED	1840	53	94	-0.8
-33C	70	CLOSED	1600	33	95	-5.0
-33D	70	CLOSED	800	40	90	-
-26C	70	CLOSED	1100	97	78	-2.2
-26C-1	70	CLOSED	1100	74	81	-4.4

*Denotes an average of two separate sheets

Continails
APPENDIX II

TABLE V

TESTS AT 400°F IN CLOSED MLO 8200/PLEKOL 201 BLENDS*

COMPOUND	FLUID	TIME	TENSILE	% ELONGATION	HARDNESS	% VOLUME CHANGE	BRITTLE POINT °F
453-26C	8200	70	1750	90	85	+0.4	-
453-26C	8200	70	-	-	-	0	-
453-26C	8200	70	1200	97	78	-2.2	-
453-26C	8200	70	1530	123	76	+1.0	-30
453-26C	90/10	70	1125	125	67	+9.8	-55
453-26C	80/20	70	1050	133	60	+20.0	-75
453-26C	70/30	70	875	133	54	+32.0	-95
453-26C	8200	168	1300	47	94	+12.7	+30
453-26C	85/15	168	650	85	63	+22.1	-57

APPENDIX II

TABLE VI

SWELL OF STANDARD STOCKS IN CLOSED MLO 8200/PLEKOL 201 BLENDS*

STOCK	FLUID	TIME	TEMP.	% VOLUME CHANGE
"L"	8200	70	250	+4.0
"L"	80/20	70	300	+22.7
"L"	75/25	70	300	+27.0
"L"	80/20	168	300	+23.1
"L"	75/25	168	300	+27.5
"R"	85/15	70	250	+26.7
"R"	85/15	70	300	+30.0
"R"	85/15	70	250	+26.3

*Blends are given same anti-oxidant concentration as MLO 8200

TRADEMARK COMPOUNDING INGREDIENTS

<u>TRADEMARK</u>	<u>USE</u>	<u>SUPPLIER</u>
Neoprene	elastomer	E. I. duPont
NA-22	accelerator	E. I. duPont
Neozone A	anti-oxidant	E. I. duPont
Thermoflex A	anti-flex- cracking agent	E. I. duPont
Aranox	anti-oxidant	Naugatuck Chemical
Trimene Base	curing agent	Naugatuck Chemical
TP-90B	plasticizer	Thiokol Corporation
Plexol	plasticizer	Rohm & Haas
Paracril	elastomer	Naugatuck Chemical