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CCL REPORT NO. 244

FINAL REPORT

INVESTIGATING FUEL-ALCOHOL EFFECTS ON ELASTOMER COMPONENTS OF DIESEL INJECTOR SYSTEMS

BY

M. E. LEPERA & C. A. VOGEL

JANUARY 1968

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U. S. ARMY COATING & CHEMICAL LABORATORY
Aberdeen Proving Ground
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ABSTRACT

An investigation was conducted to define possible deleterious effects on injector system "o-ring" components resulting from additions of freeze-point depressants to diesel fuel. An accelerated test method was subsequently developed to determine the compatibility of fuel-alcohol mixtures with a variety of molded "o-ring" components currently in use by equipment manufacturers. It was found that as low as three percent additions of ethanol to diesel fuel resulted in significant losses in elastomer properties. In addition, the incorporating of a stress mode of exposure enhanced the degradatory effects of alcohol-fuel mixtures or the test "o-ring" components.

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DEPARTMENT OF THE ARMY
U. S. ARMY COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND, MARYLAND 21005

M. E. LePera/kwl/3367

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26 February 1968

SUBJECT: CCL Report ... 44, Investigating Fuel-Alcohol Effects on Elastomer Co... nents of Diesel Injector Systems

TO: Defense Documentation Center
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The following pen ink changes should be made to subject report:

a. Page 12, Table III - under "Volume Change %" on line 11, the value for "BX-2" in "DF-2" should read "6.2" instead of "10.1".

b. Page 12, Table III - under "Volume Change %" on line 14, the value for "CP-1" in "DF-2" should read "18.8" instead of "28.4".

c. Page 12, Table III - under "Volume Change %" on line 15, the value for "CP-1" in "DF-2 + 3% ROH" should read "28.4" instead of "0.1".

FOR THE COMMANDER:

H. L. Ammlung

H. L. AMMLUNG
Deputy Technical Director

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I. INTRODUCTION

The effective operation of current automotive machinery requires the mechanical seal protection given by elastomeric o-rings. The selection of "o-ring" elastomer type is dependent upon the specific environmental conditions (1); namely, temperature, solvent media, and seal design requirements. In diesel injector systems, nitrile rubber (designated as "NBR") normally provides satisfactory service for a variety of hydrocarbon fuels under both static and dynamic operating conditions. Operation of diesel powered vehicles in arctic environments presents serious problems attributed to the formation of "condensate" water, resulting in plugged filters and/or fuel lines. This problem has been lessened, to some extent, in gasoline powered systems by additions of low molecular weight alcohols to the fuel (2); however, the application of these alcohols, functioning as freeze-point depressants, for use in diesel powered equipment, has not been as extensive as compared to gasoline powered equipment.

In order to anticipate possible field problems resulting from the additions of alcohol to diesel injector systems, a program was subsequently conducted at Development & Proof Services, Aberdeen Proving Ground, Maryland. Using a Bacharach Fuel Injector Calibration Stand, the results obtained indicated (3) no problems to occur from additions of up to 10% ethanol (absolute grade) to diesel fuel in terms of flow control, injector seizure, or wear tendencies. However, disassembly of the bench scale injector pump revealed significant deterioration of NBR "o-ring" components. Similar experience of leaking "o-rings" in the fuel dispensing unit (burets) of this injector tester were also observed

In order to define the extent of this possible incompatibility, a program was initiated to determine the effects of additions of alcohols to petroleum fuels on molded "o-ring" components of different compositions. It should be noted that the specific types of "o-ring" materials selected have satisfactory resistance to diesel and other petroleum fuels as well as having a marginal resistance to alcohols. The extent of deterioration was determined by comparative exposure of sample materials to hydrocarbon and hydrocarbon-alcohol mixtures under fixed test conditions using volume change, hardness, and tensile strength measurements.

II. DETAILS OF TEST

A. Background.

Fluid resistance of elastomers are currently determined by direct immersion of the elastomer sample in a specified test fluid as outlined (4) in ASTM D 471-63T (Changes in Properties of Elastomeric Vulcanizates Resulting From Immersion in Liquids). This method is designed to evaluate the comparative ability of a rubber or elastomeric specimen to withstand the effects of fluids by evaluation of the sample before and after specified exposure periods. Such measurements as percent volume increase, drop in tensile strength and hardness characterize the ability of the elastomer to be resistant to the test fluid during the required exposure period. Owing to the wide variations of time-temperature conditions usually present in operational environments, no direct correlations between this static immersion and service performance may be given or implied. However, this test provides comparative data for predicting service performance and is especially useful in research and development work. In general, this test recommends one of eight "standard" temperatures, ranging from 23 ± 1.1° to 250 ± 1°C., and one of four immersion periods, ranging from 22 ± 2 hours to 28 days, depending upon the anticipated service requirement. From the standpoint of simulating actual service conditions, any static immersion test would be inadequate. Since a literature survey revealed no laboratory procedures for evaluating the effects of alcohol-hydrocarbon environments on elastomer specimens, a static immersion test was developed to define possible deleterious effects.

B. Development of the Standard Immersion Test.

In order to establish "realistic" test conditions, evaluations consisting of various fuel-alcohol level, diesel fuel and alcohol types, temperature variations, and exposure times were performed using 1 square inch samples cut from 1/16" calandared nitrile rubber sheetstock. The sheetstock material was utilized for developing the test conditions of the immersion test for reasons of materiel availability and uniformity of composition due to calandaring processes. The static immersion tests were conducted by exposing the elastomer sample in sealed wide-mouth screw-cap jars (430 ml. capacity) containing 200 ml of test fluid. The fuels initially evaluated were as follows:

1. Military Specification MIL-F-45121B, (CITE.R) Fuel, Compression Ignition and Turbine Engine, Referee Grade.

2. Military Specification MIL-T-5624G, Turbine Fuel, Aviation Grade JP-5.

3. Federal Specification VV-F-800a, Fuel Oil, Diesel, Grades DF-2 (Regular), and DF-A (Arctic).

4. Federal Specification TT-S-735, Standard Test Fluid, Hydrocarbon, Type II (Iso-octane and aromatic mixture).

5. Caterpillar 1-H Engine Test, Reference Grade Diesel Fuel.

The alcohols tested were absolute ethanol, methyl cellusolve (ethylene glycol mono methyl ether), and isopropanol. Methanol was not evaluated due to its limited solubility in diesel fuels. For evaluation of ethanol in DF-2, additions of alcohol in concentrations (% volume) of nil, 1%, 3%, 6%, 10%, 20% were employed. For other fuel-alcohol evaluations, the alcohol component was fixed at the 3% level. Exposure conditions varied from 8 to 137 hours at 70°C., 16 hours at 100°C., and 1 week at room temperature. Before and after exposure, the NBR specimens were evaluated for hardness decrease and change in volume. The results of variation of exposure media and test duration obtained using the nitrile rubber sheetstock material in terms of volume increase and hardness change are given in Tables I and II (see Appendix A).

The results of these tests indicated the maximum distending of nitrile rubber to occur after a 16-hour exposure period at 70°C. in a diesel fuel containing 3%(vol) ethanol. Utilizing these "selected" standard conditions, additional evaluations were made with representative moulded o-ring components obtained from injector and diesel engine manufacturers. The results obtained are given in Table III (see Appendix A). For the evaluation of these "o-rings" of varied geometry, it was found that o-rings, having size configurations of approximately 2 inch I.D. and .300 inch cross section were satisfactory with respect to sample requirements for available testing equipment. In addition, the ratio of exposed surface to fuel volume for "o-rings" of the above configuration correlated with that ratio for the NBR sheetstock specimens.

Standard size o-rings of 2.122 in I.D. and .308 inches cross sectional area of the following types were obtained from a commercial supplier:

1. nitrile rubber - low acrylonitrile content
2. nitrile rubber - medium acrylonitrile content
3. nitrile rubber - high acrylonitrile content
4. neoprene
5. viton A
6. fluorosilicon
7. polysulfide

The individual o-ring types were evaluated in duplicate, excepting the fluorosilicon, under the conditions of the standard immersion test (see Test Procedure 1, Appendix B). The effects of this exposure period on the respective "o-rings" swell, tensile strength, and hardness changes are tabulated in Table IV. It should be noted that the individual properties of each "o-ring" type were included in Table IV for comparison purposes. Hydrin 200, a copolymer of epichlorohydrin and ethylene oxide reported (5) to have excellent fuel resistance, was also evaluated and the results included in Table IV; however, due to its non-availability in the required "o-ring" size configuration, the respective evaluation tests were conducted on one square inch specimens and standard dumbbells.

C. Evaluation of "O-rings" Types Under Stress Conditions.

Although it was beyond the scope of this work to determine the serviceability of different "o-ring" types under conditions of dynamic operation, a simple stress-immersion test was desired to provide additional information relating to alcohol-fuel solubility interactions. Due to the complexity of apparatus required for the dynamic testing of "o-ring" components, a test to define additional effects of exposure media resulting from evaluating elastomers under conditions of stress (elongation) was developed. Essentially, the conditions of the standard immersion test were repeated with the individual "o-ring" specimen being evaluated under a stretched configuration on a stainless steel bar; namely, the amount of stretch (or stress) being ca. 28% elongation. Details of this test modification are given in Appendix B. It should be noted that the inclusion of this "stress test" would, in addition to the defining of effects resulting from exposure under stressed conditions, enable the determining of any permanent set tendencies. The six "o-ring" types were subsequently evaluated in the standard immersion test under 28% elongation, and the results obtained are given in Table V (see Appendix A). To illustrate the effects produced by additions of alcohol to the two exposure tests, a tabulation was prepared to show any significant changes in physical properties and the results are given in Table VI (see Appendix A).

III. RESULTS OF TEST

The initial evaluations of the nitrile rubber sheetstock specimens resulting from fuel-alcohol interactions revealed the following trends:

A. Of all fuels tested, DF-2 produced the greatest degree of swell (a maximum of 10%) and hardness decrease (10%) at 70°C.

B. A 3%(vol.) addition of absolute ethanol to DF-2 resulted in a twofold increase in volume (maximum being realized after 12 hours at 70°C.). In addition, the resultant hardness decrease was 17% after 4 days at 70°C. This apparent ethanol-diesel fuel synergism is similar to that reported (6) for natural rubber in hexane-ethanol and for nitrile rubber in benzene-methanol (7).

C. With higher exposure temperatures (100°C. versus 70°C.), there was a smaller increase in volume (one-fourth less than that observed at 70°C.) after exposure to the DF-2 containing 3% ethanol. Hardness decrease, however, was enhanced at the elevated test temperatures as an additional one-third decrease above the 70°C. condition was realized.

D. Increasing the alcohol content produced a gain in the swelling tendency and significant decreases in hardness. The swell increase, however, was proportionally less for increasing alcohol content.

Samples of "o-ring" parts obtained from commercial fuel injector manufacturers permitted on evaluation of representative materials currently in use. More specifically, those parts demonstrating poor resistance to alcohol-fuel mixtures would be indicative of potential problem areas requiring additional investigation. These "o-rings" primarily consisted of nitrile rubber of unknown compounding specifications for proprietary reasons. Most of the results obtained on the nitrile rubber o-rings followed those previously determined for the sheetstock specimens. However, a "shape-size" factor gave uncorrelatible results which the following exemplifies:

A. Two identical "o-rings" (Part No. BX-2) were exposed for 16 hours at 70°C. in 100 ml. and 900 ml. total volume solutions of 3% ethanol in DF-2 respectively. After exposure, the "o-ring" from the 100 ml. solution had a 16.5% increase in volume and a final tensile strength of 3340 psi. (initial tensile strength being 4160 psi.) whereas the "o-ring" from the 900 ml. solution had a 19.4% increase in volume and a final tensile strength of 2380 psi.

B. The small "o-rings" (Part No. CU-2) showed low swell but a significant variation in test results under identical exposure conditions. It should be noted that, due to its small size, this o-ring sample (Part No. CU-2) has a relatively high surface to volume ratio with small mass which would possibly permit an intermediate "equilibrium" condition to occur prior to weighing, testing, etc. that was unobserved in the larger "o-ring" exposure tests. This potential variation of results supplemented the standardizing on the larger "o-ring" size configurations.

Standard Immersion Test. The percent swell and change in physical properties varied widely among the "o-ring" types. The volume change was rather consistent in duplicate runs, usually within a percent, based upon a 100% change. The high variability between samples in original tensile strength seems to indicate the differences may be either inherent experimental error or manufacture variability rather than exposure test differences.

Of the "o-rings" tested, all types except neoprene appeared to be suitable for use in diesel fuel. The Viton had the lowest swell in the diesel fuel-alcohol mixture, followed by fluorosilicon, polysulfide, and the nitrile rubber. The percentage of original properties retained parallel to some degree, the results obtained for percent swell increase with the exception of fluorosilicone; namely, its low retention of tensile strength in DF-2 containing 3% ethanol. However, the low initial tensile strength of fluorosilicone and polysulfide make their desireability questionable.

The nitrile results were not completely dependent upon the acrylonitrile level. The high acrylonitrile gave the lowest swell in diesel fuel and the highest swell in the alcohol-diesel mixture whereas the low acrylonitrile had the highest swell in diesel fuel with the lowest in alcohol-diesel mixture. Similar trends were followed in percent of original hardness and retention of tensile strength; however, the tensile strength and swell results of the nitrile-medium acrylonitrile content did not fall between the high acrylonitrile and low acrylonitrile as was anticipated. With the exception of the Viton and polysulfide, the nitriles retained the highest percentage of their original properties. The low acrylonitrile was best in this respect, although only marginally, and had the lower tensile strength of all the nitriles evaluated.

The swell characteristics of Hydrin 200 were comparable to high acrylonitrile NBR. Its initial experimental tensile strength of 1700 psi was somewhat lower than its reported (8) 2050 psi. Its retention of tensile strength in alcohol-diesel fuel mixture was good but its comparative retention in DF-2 alone was relatively poor. The specimen difference existing between slab versus "o-ring" plus non-duplicate determinations make comparison of results between Hydrin 200 and that of the standard "o-rings" questionable.

Evaluation of the standard "o-rings" under the stress of approximately 28% elongation revealed the following significant trends:

A. Greater swell resulted.

B. Less retention of original tensile strength.

C. More of the original hardness retained.

It was observed that the polysulfide samples had much poorer retention of physical properties under these "stressed" conditions. Although Viton maintained nearly all its original properties after exposure to this "stress" modification, a very severe tension and compression set was observed to have resulted. For the nitriles, the swell and hardness results were as before. Yet when tested under stress, the high acrylonitrile maintained the greatest percentage of original tensile strength; namely, approximately 68% compared to the low acrylonitriles approximately 59% in the alcohol-diesel fuel mixture.

Work recently conducted at Rock Island Arsenal (8) involving the investigation of elastomer compatibility with various fluids revealed similar results as were obtained by this Laboratory. To illustrate this point and to also provide supplemental information, the results of evaluating representative elastomers for 70 hours at 212°F. in MIL-F-25524A (Fuel, Aircraft Turbine and Jet Engine, Thermally Stable) are shown on Table VI (see Appendix A). It should be noted that polyurethanes were not included in their investigation because of the reported (9, 10) poor resistance to alcohols. To further illustrate the possible incompatibility of fuel-resistant elastomers with alcohol-fuel mixtures, selected data was obtained from a recent publication (11) and the results are given in Table VII (see Appendix A). It is evident that elastomers having satisfactory alcohol resistance usually have unsatisfactory resistance to hydrocarbon fuels.

IV. CONCLUSIONS

A test procedure was developed to determine the compatibility of alcohol-diesel fuel mixtures with elastomeric materials currently used in injector fuel systems. It was found that test conditions of 16 hours at 70°C. with exposure to diesel fuel containing 3% ethanol resulted in the greatest loss of elastomeric properties for nitrile rubber samples. The effect of the alcohol-diesel fuel mixture was significantly more severe than diesel fuel alone for most elastomer components tested. The results obtained with the representative "o-ring" samples indicate that a potential problem area may exist where the frequent addition of alcohol is required. A stress-immersion test was utilized to define additional deleterious effects resulting from exposure of elastomers under stress conditions. Viton had the best retention of physical properties, but its tendency to form permanent set resulting in marginal dynamic-seal capabilities make its selection somewhat questionable. Considering the maximum retention of physical properties after testing, the polysulfide and fluorosilicon would seem satisfactory; however, both elastomer types had low initial physical properties and the polysulfide demonstrated tendencies towards permanent set under the stress conditions.

It should be recognized that such physical property measurements yield empirical values which may be misleading for the prediction of "o-ring" performance capabilities. The ultimate requirements for determining or predicting satisfactory performance of elastomer parts would necessitate their evaluation in actual field hardware environments. However, a recent publication (12) provides a physio-chemical approach for the prediction of elastomer-fluid compatibility by the determining of three specific solvency indexes; namely, solubility parameter, hydrogen bonding, and dipole moment.

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15. Military Specification MIL-F-25524A Fuel, Aircraft Turbine and Jet Engine Fuel, Thermally Stable.

16. Military Specification MIL-F-45121B (CITE.R) Fuel, Compression Ignition and Turbine Engine, Referee Grade.

17. Federal Specification TT-S-735, Standard Test Fluid; Hydrocarbon, Type II (Iso-octane and aromatic mixture).

18. Federal Specification VV-F-800a, Fuel Oil, Diesel Grades DF-A (Arctic Grade) and DF-2 (Regular Grade).

APPENDIX A

TABLE I

FUEL-ALCOHOL EFFECTS ON NITRILE RUBBER SHEETSTOCK SAMPLES EXPOSED AT 70°C.

Fuel Evaluated	Alcohol Added, % Volume	Exposure Time (Hrs)	% Change In Volume	Durometer Hardness Change (Shore A Points)
VV-F-800, DF2	(neat)	8	7.7	-7
VV-F-800, DF2	Ethanol, 3%	8	20.9	-11
VV-F-800, DF2	(neat)	16	9.0	-6
VV-F-800, DF2	(neat)	16	6.1	-7
VV-F-800, DF2	Ethanol, 3%	16	21.4	-13
VV-F-800, DF2	Ethanol, 10%	16	26.2	-16
VV-F-800, DF2	Ethanol, 20%	16	31.3	-19
VV-F-800, DF2	(neat)	24	11.0	-8
VV-F-800, DF2	Ethanol, 3%	24	21.0	-8
VV-F-800, DF2	(neat)	48	10.9	-10
VV-F-800, DF2	Ethanol, 1%	48	14.4	-10
VV-F-800, DF2	Ethanol, 3%	48	20.4	-14
VV-F-800, DF2	Ethanol, 6%	48	25.8	-14
VV-F-800, DF2	(neat)	68	10.2	-10
VV-F-800, DF2	Ethanol, 3%	68	19.5	-12
VV-F-800, DF2	Cellusolve, 3%	68	20.7	-14
VV-F-800, DF2	Isopropanol, 3%	68	17.5	-14
VV-F-800, DF2	(neat)	94	10.2	-10
VV-F-800, DF2	Ethanol, 3%	94	18.4	-14
VV-F-800, DF2	(neat)	137	9.8	-10
VV-F-800, DF2	Ethanol, 3%	137	18.2	-14
VV-F-800, DFA	(neat)	48	6.8	-8
VV-F-800, DFA	Ethanol, 3%	48	14.0	-11
MIL-T-5624G	(neat)	24	4.0	-8
MIL-T-5624G	(neat)	68	3.9	-7
MIL-T-5624G	Ethanol, 3%	68	9.2	-11
MIL-T-5624G	Cellusolve, 3%	68	9.8	-10
MIL-F-45121B	(neat)	48	5.7	-5
MIL-F-45121B	Ethanol, 3%	48	13.6	-11
MIL-F-45121B	Cellusolve, 3%	48	13.6	-10
MIL-F-45121B	Isopropanol, 3%	48	11.8	-10
MIL-F-45121B	(neat)	68	4.5	-7
MIL-F-45121B	Ethanol, 3%	68	11.0	-10

TABLE I (CONTINUED)

Fuel Evaluated	Alcohol Added, % Volume	Exposure Time (Hrs)	% Change In Volume	Durometer Hardness Change (Shore A Points)
1-H Diesel	(neat)	68	2.6	-7
1-H Diesel	Ethanol, 3%	68	9.5	-9
1-H Diesel	Cellusolve, 3%	68	11.1	-11
TT-S-735, II	(neat)	48	16.1	-12
TT-S-735, II	Ethanol, 3%	48	24.5	-16

TABLE II

FUEL-ALCOHOL EFFECTS ON NITRILE RUBBER SHEETSTOCK SAMPLES

Fuel Evaluated	Alcohol Added, % Volume	Exposure Conditions	% Change In Volume	Durometer Hardness Change (Shore A Points)
VV-F-800, DF2	(neat)	16 hrs/100°C.	7.1	-10
VV-F-800, DF2	Ethanol, 3%	16 hrs/100°C.	15.1	-14
VV-F-800, DF2	Cellusolve, 3%	16 hrs/100°C.	21.7	-16
VV-F-800, DF2	Ethanol, 6%	16 hrs/100°C.	21.5	-13
VV-F-800, DF2	(neat)	16 hrs/100°C.	7.3	-7
VV-F-800, DF2	Ethanol, 2%	16 hrs/100°C.	10.9	-10
VV-F-800, DF2	Isopropanol, 3%	16 hrs/100°C.	10.8	-10
MIL-F-45121B	(neat)	16 hrs/100°C.	6.2	-5
VV-F-800, DF2	(neat)	7 days/25°C.	6.5	-5
VV-F-800, DF2	Ethanol, 3%	7 days/25°C.	22.9	-13
MIL-F-45121B	(neat)	7 days/25°C.	6.2	-6
MIL-F-45121B	Ethanol, 3%	7 days/25°C.	13.1	-10
TT-S-735, II	(neat)	7 days/25°C.	16.6	-8
TT-S-735, II	Ethanol, 3%	7 days/25°C.	20.9	-13

TABLE III

FUEL-ALCOHOL EFFECTS ON "O-RINGS" OBTAINED FROM EQUIPMENT SUPPLIERS AFTER EXPOSURE AT 70°C.

Part Designation[1]	Exposure Media	Test Duration	Volume Change %	Tensile Strength Retained %	Hardness Change Pts.
BX-1	DF2	16 hours	8.3	96.8	-4
BX-1	DF2 + 3% ROH	16 hours	22.0	54.9	-9
BX-1	DF2	62 hours	12.6	83.9	-7
BX-1	DF2 + 3% ROH	62 hours	21.7	87.2	-20
CU-1	DF2	16 hours	26.2	58.7	-5
CU-1	DF2 + 3% ROH	16 hours	19.8	70.8	-4
CU-2	DF2	16 hours	6.6	100.0	-1
CU-2	DF2	16 hours	5.7	77.8	-4
CU-2	DF2 + 3% ROH	16 hours	0.9	64.7	-4
CU-2	DF2 + 3% ROH	16 hours	12.8	77.3	-13
BX-2	DF2	16 hours	10.1	(3960)	-10
BX-2[2]	DF2 + 3% ROH	16 hours	16.5	(3335)	-18
BX-2[3]	DF2 + 3% ROH	16 hours	19.4	(2380)	-19
CP-1	DF2	16 hours	28.4	82.2	-2
CP-1	DF2 + 3% ROH	16 hours	0.1	78.5	-4
BO-1	DF2	16 hours	0.1	(3240)	-2
BO-1	DF2 + 3% ROH	16 hours	-3.5	(3500)	-4

[1] Initial Properties of O-Ring Samples were:

Part No.	Ten. Strength	Hardness	O. D.	Cross-Section Area	Elastomer Materiel
BX-1	2045	69	2.00"	0.01515	NBR
CU-1	3560	63	1.20"	0.00422	NBR
CU-2	4360	67	1.25"	0.00362	NBR
BX-2	N. D.	73	2.35"	0.03362	NBR
CP-1	3210	64	0.75"	0.00873	NBR
BO-1	N. D.	68	0.75"	0.00468	VITON

[2] Total Volume of exposure media being 100 ml.

[3] Total Volume of exposure media being 900 ml.

NOTE: Total Volume of media for standard immersion test is 200 ml.

TABLE IV

FUEL-ALCOHOL EFFECTS ON SELECTED STANDARD O-RINGS AFTER EXPOSURE TO STANDARD IMMERSION TEST[1]

Elastomer Type[3]	Exposure Media	Volume Change %	Hardness Change Pts.	Tensile Strength Retained, %
Nitrile - low acrylonitrile	DF2	13.7	-6	105
Nitrile - low acrylonitrile	DF2 + 3% ROH	22.3	-12	77.9
Nitrile - medium acrylonitrile	DF2	14.0	-9	79.5
Nitrile - medium acrylonitrile	DF2 + 3% ROH	25.4	-12	69.7
Nitrile - high acrylonitrile	DF2	12.8	-7	88.0
Nitrile - high acrylonitrile	DF2 + 3% ROH	27.3	-12	73.7
Neoprene	DF2	57.5	-8	43.9
Neoprene	DF2 + 3% ROH	62.7	-12	42.8
VITON	DF2	0.5	-1	109
VITON	DF2 + 3% ROH	3.8	-2	92.2
Fluorosilicon	DF2	5.6	0	93.6
Fluorosilicon	DF2 + 3% ROH	7.3	-1	59.6
Polysulfide	DF2	7.0	-4	90.4
Polysulfide	DF2 + 3% ROH	13.2	-8	82.2
HYDRIN 200[2]	DF2	13.0	--	--
HYDRIN 200	DF2 + 3% ROH	26.3	--	--

[1]Exposure conditions being 16 hours at 70°C.

[2]Results obtained from samples cut from calandered stock.

[3]Initial Properties of Standard O-Rings were as follows:

Elastomer Type	Tensile Strength, psi	Hardness
HYDRIN 200	1700	62
Nitrile - low acrylonitrile	1610	68
Nitrile - medium acrylonitrile	2140	67
Nitrile - high acrylonitrile	2360	69
Neoprene	2330	67
VITON	1130	68
Fluorosilicon	760	55
Polysulfide	590	63

TABLE V

FUEL-ALCOHOL EFFECTS ON SELECTED STANDARD O-RINGS (UNDER STRESS) AFTER EXPOSURE TO STANDARD IMMERSION TEST[1]

Elastomer Type[2]	Exposure Media	Volume Change %	Hardness Change Pts.	Tensile Strength Retained, %
Nitrile - low acrylonitrile	DF2	18.1	-4	100
Nitrile - low acrylonitrile	DF2 + 3% ROH	26.3	-7	58.6
Nitrile - medium acrylonitrile	DF2	16.4	-4	81.8
Nitrile - medium acrylonitrile	DF2 + 3% ROH	28.4	-9	54.5
Nitrile - high acrylonitrile	DF2	16.1	-4	90.7
Nitrile - high acrylonitrile	DF2 + 3% ROH	30.6	-10	68.1
Neoprene	DF2	64.6	-9	40.4
Neoprene	DF2 + 3% ROH	69.7	-11	40.4
VITON	DF2	0.7	0	106
VITON	DF2 + 3% ROH	3.9	-4	83.5
Fluorosilicon	DF2	6.4	+1	85.2
Fluorosilicon	DF2 + 3% ROH	7.9	-1	59.6
Polysulfide	DF2	6.5	-4	(broke)
Polysulfide	DF2 + 3% ROH	13.5	-8	60.3

[1]Exposure conditions being 16 hours at 70°C. with o-ring tested at 28% constant elongation.

[2]Initial Properties of Standard O-Rings were as follows:

Elastomer Type	Tensile Strength, psi	Hardness
Nitrile - low acrylonitrile	1610	68
Nitrile - medium acrylonitrile	2140	67
Nitrile - high acrylonitrile	2360	69
Neoprene	2330	67
VITON	1130	68
Fluorosilicon	760	55
Polysulfide	590	63

TABLE VI

DIFFERENCE IN PHYSICAL PROPERTIES OF STANDARD O-RINGS RESULTING FROM ADDITIONS OF ETHANOL

Elastomer Type	Test Conducted	Difference of Value Percentages in: Volume Change	Ten. Strength	Hardness
Nitrile - low	Std. Immer. Test	+8.6%	-37.1%	-6
Nitrile - low	Std. Immer. Test - Stressed	+8.2%	-41.4	-3
Nitrile - med.	Std. Immer. Test	+11.4%	-9.8%	-3
Nitrile - med.	Std. Immer. Test - Stressed	+12.0	-27.3%	-5
Nitrile - high	Std. Immer. Test	+14.5%	-29.8%	-5
Nitrile - high	Std. Immer. Test - Stressed	+14.5	-22.6	-5
Neoprene	Std. Immer. Test	+5.2%	-1.1%	-4
Neoprene	Std. Immer. Test - Stressed	+5.1	-27.7	-2
VITON	Std. Immer. Test	+3.3%	-16.8%	-1
VITON	Std. Immer. Test - Stressed	+3.2	-22.5	-4
Fluorosilicon	Std. Immer. Test	+1.7%	-34.0%	-1
Fluorosilicon	Std. Immer. Test - Stressed	+1.5%	-25.6	-2
Polysulfide	Std. Immer. Test	+6.2%	-8.2	-4
Polysulfide	Std. Immer. Test - Stressed	+7.0	--	-4

TABLE VII

PHYSICAL PROPERTY CHANGES[1] OF ELASTOMER VULCANIZES AFTER EXPOSURE TO MIL-F-25524A (THERMALLY STABLE JET FUEL) FOR 70 HOURS AT 212°F.

Elastomer Tested[2]	Volume Change, %	Hardness Change, %	Tensile Strength Change, %	Elongation Change, %
Paracril A	+25	-14	-29	-30
Paracril B	+13	-7	-17	-32
SBR 1023	+154	-39	-92	-65
Enjay Butyl 325	Severe	-47	-93	-75
Nordel 1070	+166	-28	-78	-59
Genthane S	+2	-1	-16	-4
Adiprene C	+16	-7	-55	-31
HYDRIN 200	+5	+2	-3	-33
SE 555U	+260	+4	-31	-93
LS-422	+11	-42	-31	-18
VITON A	+3	0	0	0

[1]Values taken from following reference:
R. A. Faord, "Compatibility of Elastomers With Hydraulic Fluids, Lubricants & Fueis", Rock Island Arsenal Report No. 67-1148, p. 14, May 1967.

[2]Elastomer types were as described as:

Paracril A:	Butadiene-Acrylonitrile (82/18)
Paracril B:	Butadiene-Acrylonitrile (74/26)
SBR 1023:	Styrene-Butadiene
Enjay Butyl 325:	Isobutylene-Isoprene Copolymer
Nordel 1070:	Ethylene-Propylene Terpolymer
Genthane S:	Polyurethane Ester
Adiprene C:	Polyurethane Ether
HYDRIN 200:	Epichlorohydrin Copolymer
SE 555U:	Silicone
LS-422:	Fluorinated Silicone
VITON A:	Vinylidiene Fluoride - Hexafluoropropylene Copolymer

TABLE VIII

PHYSICAL PROPERTY CHANGES[1] OF ELASTOMERS AFTER EXPOSURE TO VARIOUS FLUIDS FOR 72 HOURS AT 212°F.

Elastomer Tested[2]	Fluid Type	Volume Change, %	Hardness Change, Pts.	Tensile Strength Change, %	Elongation Change, %
Enjay Butyl 218	Ethanol	+2.1	-3	91.0	82.9
Enjay Butyl 218	Isopropanol	+2.4	-3	89.8	91.6
Enjay Butyl 218	ASTM Fuel A	+159.0	-40	18.1	25.5
Enjay Butyl 218	ASTM Fuel C	+233.0	-47	13.3	21.0
Enjay Butyl 035	Ethanol	+1.5	-3	90.3	88.7
Enjay Butyl 035	Toluene	+309.0	-53	69.9	26.9
Enjay Butyl HT 10-66	Ethanol	+4.9	-1	92.4	72.9
Enjay Butyl HT 10-66	Prem. Gasoline	+167.0	-34	21.7	28.9
Enjay Butyl HT 10-66	Toluene	+238.0	-41	17.7	29.9
Natural Rubber	Ethanol	+2.4	0	78.4	58.4
Natural Rubber	Toluene	N.A.	N.A.	N.A.	N.A.
Styrene-Butadiene Rubber	Ethanol	-0.1	+3	70.9	47.3
Styrene-Butadiene Rubber	Toluene	+256.0	-38	11.1	18.4
Butadiene-Acrylonitrile Rubber	Ethanol	+22.3	-10	52.6	49.8
Butadiene-Acrylonitrile Rubber	Prem. Gasoline	+29.1	-16	62.9	62.9
Butadiene-Acrylonitrile Rubber	Toluene	+125.0	-31	10.7	17.0
Polychloroprene (Neoprene)	Ethanol	+2.9	-4	85.6	79.4
Polychloroprene (Neoprene)	Prem. Gasoline	+69.6	-28	41.2	58.3
Polychloroprene (Neoprene)	Toluene	+209.0	-44	15.9	37.2
HYPALON	Ethanol	+4.8	-6	81.1	82.1
HYPALON	Prem. Gasoline	105.0	-30	25.4	53.1
HYPALON	Toluene	+171.0	-37	17.8	36.2

[1] Values taken from "Enjay Butyl Rubber Resistance Handbook".

[2] Elastomer Types were: (a) Butyl 218: Isobutylene-isoprene copolymer; (b) Butyl 035: Isobutylene-isoprene copolymer (low unsaturation); (c) Butyl HT 10-66: Chlorinated isobutylene-isoprene copolymer.

APPENDIX B

STANDARD IMMERSION TEST

1. Scope. This method is designed for evaluating the compatibility of elastomer o-rings with hydrocarbon and hydrocarbon-alcohol mixture in terms of physical property changes; namely volume change, tensile strength loss, and hardness decrease. This method provides for the evaluating of o-rings under conditions of stress (in a stretched configuration) as well as the normal relaxed condition.

2. Outline of Method. O-rings of a specified size are exposed for 16 hours at 70°C. (158°F.) in a diesel fuel (or other distillate-type fuels) and diesel fuel containing 3%(vol) ethanol media respectively. After termination of test, physical property measurements are determined to evaluate the effects of the two test media. Concurrent with this, similar o-rings are exposed in identical media under stress conditions (constant 28% elongation) to permit the defining of additional deleterious effects resulting from the stressed exposure conditions.

3. Specimen. Selected elastomer o-rings having reported fuel-resistance should conform to the following dimensions: 2.12 inch I.D. with 0.308 square inch cross sectional area.

4. Apparatus.

a. Scott Tester, 0 to 500 lbs. capacity, Model J-2, for determining tensile strength measurements.

b. Durometer Hardness Gauge, Type A, for determining "Shore Hardness" measurements.

c. Glass Jar, Clear, wide-mouth, screw-cap, 430 ml. capacity, metal lid fitted with VITON AHV gasket liner.

d. Glass Jar, Clear, wide-mouth, screw-cap, 235 ml. (8-ounce) capacity, metal lid fitted with VITON AHV gasket liner.

e. Stainless steel stretch bar, 4-1/2" L x 1/2" W x 1/8" T, with ends filed to give a slight concave curvature.

f. Ethyl alcohol, USI Absolute, Reagent Quality.

g. Diesel Fuel meeting VV-F-800a Fuel Oil, Diesel.

5. Procedure. Prior to any exposure testing, the selected o-ring specimens are initially evaluated for their tensile strength (ASTM D-4111 for ring samples) and durometer hardness (ASTM D-3021) to provide

base line data. With respect to durometer hardness measurements, care should be taken to indent at the center of the o-ring to minimize erraneous readings resulting from insufficient sample thickness.

a. Standard Immersion Test. For a sample o-ring evaluation, two individual (identical) o-ring specimens are required. Initially, both o-rings are individually weighed in air and water prior to exposure under accelerated aging conditions. The weighed o-ring specimens are then placed in the 430 ml. glass jars. Two-hundred milliliters of diesel fuel are then added to the first jar which is then sealed with the VITON fitted screw-cap. One-hundred and ninety-four milliliters of diesel fuel and 6 ml. of ethyl alcohol (3% vol. ethyl alcohol in diesel fuel) are subsequently added to the second jar which is then sealed with the VITON fitted screw-cap. The two sealed sample jars are placed in a constant-temperature, forced-draft oven maintained at 70°C. (158°F.) for 16 hours. After removing the jars from the oven and allowing to cool for approximately 1/2 hour, the exposed o-ring specimens were removed from their test media and allowed to equilibrate at room temperature for approximately one hour. Each o-ring was then wiped free of surface wetness with absorbant paper and immediately weighed in air and water for swell measurements. Following this, the hardness and tensile strength measurements were performed.

b. Standard Immersion Test - Stressed Condition. For a sample o-ring evaluation, two individual (identical) o-ring specimens are required. Initially, both o-rings are individually weighed in air and water prior to exposure under accelerated aging conditions. The weighed o-rings are then individually positioned under stress (28% elongation) on the 4-1/2" stretch bars and each assembly is positioned in the 235 ml. glass jar. Two-hundred and thirty milliliters of diesel fuel are then added to the first jar which is then sealed with the VITON fitted screw-cap. In the second jar, 223.1 ml. of diesel fuel and 6.9 ml. of ethyl alcohol (3% vol. ethyl alcohol in diesel fuel) are subsequently added which is then sealed with the VITON fitted screw-cap. The two sealed sample jars are placed in a constant-temperature, forced-draft oven maintained at 70°C. (158°F.) for 16 hours. After removing the jars from the oven and allowing to cool for approximately 1/2 hour, the exposed o-ring specimens were removed from the test media and stretch bars and then allowed to equilibrate at room temperature for approximately one hour. Each o-ring was then wiped free of surface wetness with absorbant paper and immediately weighed in air and water for swell measurements. Following this, the hardness and tensile strength measurements were performed.

6. <u>Calculations</u>.

a. The percent increase in volume (swell) is determined by the following:

$$\% \text{ Volume Change} = \frac{(W_{2a} - W_{2w}) - (W_{1a} - W_{1w})}{(W_{1a} - W_{1w})} \times 100$$

Where W_{1a} = weight o-ring in air before exposure

W_{1w} = weight o-ring in water before exposure

W_{2a} = weight o-ring in air after exposure

W_{2w} = weight o-ring in water after exposure

b. The tensile strength measurement was determined by the following:

$$\text{Tensile strength (psi)} = \frac{\text{Scale Reading on Scott Apparatus}}{\text{Cross Sectional Area of O-Ring}}$$

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13 ABSTRACT

An investigation was conducted to define possible deleterious effects on injector system "o-ring" components resulting from additions of freeze-point depressants to diesel fuel. An accelerated test method was subsequently developed to determine the compatibility of fuel-alcohol mixtures with a variety of molded "o-ring" components currently in use by equipment manufacturers. It was found that as low as three percent additions of ethanol to diesel fuel resulted in significant losses in elastomer properties. In addition, the incorporating of a stress mode of exposure enhanced the degradatory effects of alcohol-fuel mixtures or the test "o-ring" components.

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