REPORT NO. F-1622

DATE 27 May 1940

SUBJECT

Compounded Rubbers and Rubber-Like Materials

for Linings in Gasoline Tanks

FR-1622

BY

NAVAL RESEARCH LABORATORY
BELLEVUE, D. C.

NRL Report No. F-1622
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NAVY DEPARTMENT

Report

on

Compounded Rubbers and Rubber-Like Materials for Linings in Gasoline Tanks

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

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Distribution:
BuAero (10)

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APPENDICES

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AUTHORIZATION

1. This problem was authorized by Bureau of Aeronautics Project Order 29-40 of 30 June 1939.

INTRODUCTION

2. On 27 February 1940 were received at this laboratory six samples of rubber or compounded rubber vulcanizates which had been prepared in view of the possible use of such materials as linings for gasoline tanks. Explanatory correspondence is attached hereto as Appendix A. Because of excellent resistance to many corrosive agents, rubber linings have long been contemplated for the protection of interior surfaces of gasoline containers. The use of rubber for this purpose is negated because of the pronounced solubility of rubber-substance in liquid hydrocarbon fuels, but in recent years synthetic rubber-like materials have appeared which are more or less free of this defect and have again aroused interest in these materials as protective coatings. Furthermore, reports have lately been circulated of new developments in self-sealing gasoline tanks, the functioning of which appears to depend upon a layer of rubber-like material. This layer may be sandwiched between the metal walls of the tank and a protective layer of gasoline resistant material, or conceivably it could be applied to the exterior of the tank. In the presence of gasoline this substance is purported to swell rapidly so that when gasoline is released upon it through a puncture, the hole is effectively closed by the resultant swelling.

3. The examination of the submitted samples embraced (1) possibility for use as self-sealing compounds, and (2) suitability for protective coatings for gasoline tanks. These samples consisted of the six previously mentioned, and a seventh, obtained two weeks after the receipt of the first, which was described as an improvement of one of the earlier specimens. They were all produced by the United States Rubber Company. The samples were black in color, flexible, in compact sheet form usually reinforced with cotton fiber, and were of various thicknesses and sizes. One sample, unlike the others, was spongy in structure and had a thickness of about 1/2 inch. When received, the materials bore identifying numbers of the United States Rubber Company. For convenience, they were renumbered at random from 1 through 7. Given below is a key to the numbering system and the weights and dimensions of the seven samples.

NRL Number	U. S. Rubber Co. No.	Size, mm	Weight, gms
1	5944-30-C	3.25 x 80 x 160	70.0
2	XM5999F1	12.5 x 165 x 185	88.5
3	61XM27	2.5 x 200 x 200	176.5
4	61XM284580	2.25 x 200 x 200	144.2
5	61XM294580	2.6 x 200 x 200	131.0
6	HVM-100	1.4 x 75 x 180	127.5
7	M5945-E	3.5 x 162 x 250	234.0

EXPERIMENTAL PROCEDURE

4. Since the materials were intended as linings for gasoline tanks, the behavior with two representative gasolines was investigated. Observations were made of the solubility of the materials in gasoline, of the effect of any dissolved matter on the lead content of leaded gasoline, and of the effect of gasoline on the samples themselves. These considerations are of prime importance if storage of liquid hydrocarbon fuel is attempted in vessels so lined, or if gasoline is to be contacted with these materials even for relatively short times, as might be the case in a plane tank. Ordinary rubber, as is well known, displays a pronounced solubility in gasoline. Some of that which dissolves, being relatively non-volatile, will eventually be deposited in the carburetor and intake manifold, on the intake valve, and may reach the combustion zone giving rise to excessive carbon formation, sticky valves, and sundry troubles commonly experienced with badly gummed gasolines. Rubber will also swell in gasoline and will shrink again to approximately the former size when freed of contact with the gasoline and allowed to dry. This swelling and contraction, together with leeching of rubber substance, tends to break the bond between the rubber coat and the metallic walls of the vessel. When this happens, not only does the vessel lose the protection of an intact coating, but the contained gasoline may become grossly contaminated with broken off and dislodged particles which can block supply lines, clog strainers, and foul moving parts of the system.

5. To determine if the submitted samples had gasoline resistivities such as would permit use as protective coatings, or if they possessed properties which might adapt them as self-sealing compounds for tanks, test specimens were prepared and contacted with gasoline. Observations were made of the condition of the specimens and of the gasoline after lapses of 3 and 30 days. Since gasolines vary in solvent effect, depending on the nature of the component hydrocarbons of the fuel, and because it was desired to observe what effect, if any, the presence of dissolved matter would have on the lead content of leaded fuels, two series of tests were set up using different gasolines. In series A, the samples were contacted with an 87 octane aviation gasoline low in aromatics, composed predominantly of paraffinic hydrocarbons, and containing lead. In series B, the gasoline was a synthetic blend of several commercially available hydrocarbons boiling in the gasoline range. Percentages of the various constituents were as follows:

Paraffins (as iso-octane)	- 34%
Naphthenes (as cyclohexane and methyl cyclohexane)	- 30%
Aromatics (as benzene, toluene and xylenes)	- 36%

Such a highly aromatic blend probably includes the extreme limit of aromatic concentration likely to be encountered in aviation base stocks or finished aviation gasolines. This blend contains no lead.

6. The size of the samples taken and the amount of gasoline used in each case was adjusted so that for each square centimeter of test sur-

face there were present 10-12 cc of gasoline. This represents approximately the surface volume relationship in a cylindrical 55 gallon tank. Thus, rectangular samples about 6 x 2 centimeters presenting 24 square centimeters of surface were completely immersed in 300 cc of gasoline contained in a 500 cc pyrex Erlenmeyer flask. These flasks were tightly closed and placed immediately in a darkened cabinet at 20-23° C. At the end of three days, the specimens were removed, allowed to air dry 1-1/2 hours until no vestige of gasoline could be detected on the surface, weighed, and the dimensions taken. Meanwhile 50 cc of each gasoline were removed and evaporated in a tared beaker at 155° C. while conducting a stream of air over the surface of the gasoline at the rate of 1 liter per second. After cooling, the amount of residue was ascertained. This is a Standard A.S.T.M. method (D381-36) for the determination of gum in gasoline. It is designed to duplicate under laboratory conditions the experience of gasoline volatilizing in the engine and indicates the amount of material which will be deposited in a motor using a gum carrying fuel.

7. After these determinations, the samples were reimmersed and allowed to remain undisturbed until 30 days had elapsed from the start of the test. At the end of this time they were removed, racked in a dust-free location, and allowed to air dry for 2-1/2 weeks to insure the removal of imbibed gasoline. They were then weighed and measured as before. The relative humidity of the laboratory at the time of the original and the last weighing was 44 and 46%, respectively, so that any condensed water film on the surface of the specimens should be approximately the same in each case. Immediately upon removal of the specimens, the gum content of the gasoline was redetermined as described before, and the amount of tetraethyl lead in the gasolines of series A estimated. Sample #7, which was received after these tests were in progress, was contacted with gasoline for only three weeks as against 30 days for the others. No observation was made after a 3-day period. In the following tables are given the dimensional and weight changes of the specimens, the gum content of the gasolines and tetraethyl lead. Where necessary, the gums are corrected for lead as directed in Army and Navy Specification AN-9530 Fuel, Aircraft Engine, 92 Octane (leaded 3-1/2 ml). Attached hereto is a photograph showing the effect of 30-day contact with gasoline on Sample #2. The remaining samples suffered no alteration which can be shown photographically to an advantage.

[redacted]

DATA OBTAINED

TABLE 1

Alterations in Gasoline Contacted with Rubber Samples
Series A - 87 Octane; Series B - Aromatic Blend

NRL No.	Fresh Gasoline Gum* Content	Fresh Gasoline Lead** Content	Fresh Gasoline Color	Contacted 3 Days Gum* Content	Contacted 3 Days Lead** Content	Contacted 30 Days Gum* Content	Contacted 30 Days Lead** Content	Contacted 30 Days Color
1a	0.0	131.2	Blue	26.8	128.6	118.0	129.8	Green
2a	0.0	131.2	Blue	36.6	128.0	41.0	128.6	Blue with light greenish cast.
3a	0.0	131.2	Blue	3.4	132.0	14.0	131.4	Green
4a	0.0	131.2	Blue	0.0	131.8	2.2	130.2	Blue
5a	0.0	131.2	Blue	0.8	131.0	0.6	132.0	Blue
6a	0.0	131.2	Blue	0.4	132.0	2.4	131.2	Blue
7a	0.0	131.2	Blue	--	--	15.4	130.2	Greenish blue
1b	0.2	--	Clear	121.4	--	163.0	--	Dirty brown
2b	0.2	--	Clear	66.4	--	67.4	--	Brownish yellow
3b	0.2	--	Clear	23.8	--	40.6	--	Orange yellow
4b	0.2	--	Clear	4.4	--	11.4	--	Brownish yellow
5b	0.2	--	Clear	4.2	--	11.2	--	Brownish yellow
6b	0.2	--	Clear	22.0	--	108.8	--	Very slight yellow cast
7b	0.2	--	Clear	--	--	35.8	--	Golden yellow

*The gum content is given in mg/100 cc; all values in series A corrected for lead.
**The lead content is given in mg of lead chromate/100 cc. These values x 0.023 = cc TEL/gal.

TABLE 2

Dimensional and Weight Changes of Rubber Samples Contacted with Gasoline

NRL No.	Test Specimen; Original, Untreated				Contacted 3 Days				Contacted 30 Days			
	Dimensions				Dimensions				Dimensions			
	l	b	t	Weight	l	b	t	Weight	l	b	t	Weight
1a	6.20	2.05	0.330	6.796	6.25	2.05	0.392	6.869	6.15	2.05	0.308	6.441
2a	6.00	1.90	1.35	4.442	5.95	1.80	1.25	4.009	5.60	1.15	1.00	3.929
3a	6.25	1.95	0.262	5.200	6.20	1.95	0.279	5.213	6.20	1.95	0.268	5.098
4a	6.15	2.05	0.231	4.749	6.15	2.00	0.249	4.748	6.20	2.05	0.234	4.753
5a	6.20	2.00	0.276	5.516	6.15	1.95	0.297	5.516	6.20	2.00	0.281	5.517
6a	6.25	2.20	0.144	3.173	6.20	2.10	0.145	3.175	6.20	2.10	0.145	3.175
7a	6.25	2.05	0.347	7.407	---	--	--		6.25	2.00	0.336	7.339
1b	6.15	2.10	0.330	7.099	6.15	2.10	0.476	7.265	6.10	2.10	0.307	6.565
2b	6.05	1.95	1.35	4.627	5.95	1.90	1.20	4.171	5.10	1.00	0.80	4.027
3b	6.15	2.00	0.264	5.097	6.15	2.10	0.319	5.239	6.05	2.05	0.253	4.911
4b	6.20	2.00	0.233	4.920	6.20	2.00	0.286	4.974	6.20	2.05	0.237	4.880
5b	6.20	2.05	0.278	5.426	6.20	2.10	0.302	5.503	6.25	2.10	0.291	5.370
6b	6.15	2.05	0.144	3.058	6.45	2.10	0.163	3.350	5.95	2.00	0.159	2.738
7b	6.20	2.05	0.350	7.583	--	--	--		6.10	2.05	0.327	7.431

All dimensions in centimeters; l = length; b = breadth; t = thickness.
All weights in grams; weight includes weight of wire loop used for handling.
Numbers 1a - 7a immersed in 87 octane, leaded; Numbers 1b - 7b, in aromatic blend.

FACTS ESTABLISHED

8. The data in Table 1 demonstrate that after 30 days' contact with the test specimens all the gasolines, except those in which were immersed Samples Nos. 4, 5, and 6 in Series A, have increased in gum beyond the specification limit of 6 milligrams of gum per 100 cc. No gasoline in Series B after a 30-day period is below 6 milligrams of gum, and the quantity of extracted material appearing as gum is in each case greater with the samples in Series B than Series A. This is to be expected, because of the enhanced solvent properties of highly aromatic blends of the type employed in Series B in contrast to the predominantly aliphatic gasoline used in Series A. There is a rough parallelism in the amount of gum extracted from corresponding specimens in the two series. Thus, gasolines 4a, 5a and 6a have the lowest gum contents of any in their series, and are matched by 4b and 5b which show the least gum of those samples contacted with the aromatic blend. Gasoline 6b shows heavy gum in contrast to 6a. Sample #6 is known to be vinylite resin. A low solubility for vinylite in aliphatic solvents was anticipated, but the marked difference of solubility in aliphatic and aromatic gasolines was unexpected. The gum remaining after the evaporation of sample 6b was lighter in color and more fluid than that from any of the other samples. At the end of three days' immersion, samples 1a, 2a, 1b, 2b, 3b and 6b had so contaminated the gasolines with soluble matter that these gasolines failed to pass specifications for existent gum.

9. Gum formation in the remainder of the samples was negligible or moderate. The presence of this dissolved material is evidenced by color changes of the gasoline, as indicated in Table 1. In Series B, higher gum contents were generally accompanied by deeper tints of brown or yellow in the gasoline. In Series A, the presence of extraneous material was manifest by a shifting of the original blue color of the dyed fuel towards the green.

10. The lead content of the leaded gasolines was unaffected by the presence of foreign material from the test specimens. Therefore, in the concentrations encountered, these dissolved substances are not reactive with lead tetraethyl.

11. Dimensional and weight changes in the samples are rather interesting. Neglecting samples 2a and 2b for the time being, and reading Table 2 in conjunction with Table 1, it is observed that all samples which showed increased gum content after 3 days' contact with gasoline were themselves increased in weight and generally were thicker. This indicates that the specimens had imbibed gasoline which process was accompanied by some swelling. The quantity of gasoline so imbibed more than offsets the loss of material dissolved into the gasoline. On this account, no balance can be drawn between the loss in weight of a specimen on the one hand, and the gain in gum content of the corresponding gasoline on the other; but, at the end of 30 days' immersion, the several specimens were allowed to air dry until imbibed solvent was removed before weighing, so a balance can be set up for gum content against weight loss. It is illuminating to observe what proportion of the extracted material actually appears as gum in the gum

determination, for this is the quantity which will likely be left in an engine using such contaminated gasolines. It is recalled that each specimen was immersed at the beginning of the test in 300 cc of gasoline and that after 3 days, 50 cc of this gasoline was removed and analyzed for gum. These gum values have been expressed in the foregoing tables in milligrams of gum per 100 cc. Therefore, the total amount of gum derivable from any single test specimen will be the gum content after 30 days (as given in Table 1) multiplied by 2-1/2 plus 1/2 the indicated gum content present per 100 cc after 3 days. This quantity can then be compared directly with the weight loss of each specimen taken from the original weight and the air dried weight after 30 days' immersion as given in Table 2. Since the gasoline soluble extractables from the rubber have a certain volatility, some of these extracts will be lost through vaporization during the gum test. Hence, the recovery of dissolved matter will not be quantitative and will not agree with the actual weight losses suffered by the specimens, but as has been stated, the material which appears as gum in the gum tests gives a truer picture of what will be deposited during engine operation than would those values calculated from the amount of material actually in solution in the gasoline.

12. Tabulated below is a comparison of the total gum derivable from a single specimen under the outlined test conditions and the amount of material actually extracted, as indicated by weight changes of the specimens. Since the total volume of gasoline in each test was 300 cc, the quantities arrived at as described above have been divided by 3 in the table below, in order to express the results in terms of milligrams per 100 cc.

TABLE 3

Sample No.	Wt. of Extractable Material Appearing As Gum Per Single Specimen; Mg/100 cc	Total Wt. of Extractable Material Per Single Specimen as Determined by Weight Loss; Mg/100 cc
1a	102.8	118
2a	40.3	171
3a	12.3	34
4a	1.8	1 (increase)
5a	0.6	0.0-1 (increase)
6a	2.0	0.0-1 (increase)
7a	15.4	23
1b	156.1	178
2b	67.2	200
3b	37.8	62
4b	10.2	13
5b	10.0	19
6b	94.3	107
7b	35.8	51

[redacted]

From the above tabulation, it is seen that only a portion of the matter actually extracted from a given test sample will remain as gum on evaporation of the gasoline. The amount so remaining probably depends largely on the volatility of the extractable, and possibly upon its oxidizability under the conditions of the gum determination. Since the several samples were compounded differently, the ratio of actual gum to extracted matter varies as might be expected from specimen to specimen.

13. Samples 2a and 2b in contrast to most of the other specimens suffered weight losses and shrinkage even after 3 days' immersion in the test gasolines. These losses were accentuated by a further immersion for 30 days. Effect of this treatment is shown in the accompanying photograph.

CONCLUSIONS

14. Of the samples of rubber or rubber-like materials submitted for test, only 4, 5 and 6 appear suitable for linings of gasoline tanks in which it is proposed to keep gasoline for any length of time. Even with these samples, contact with highly aromatic gasolines should be avoided. Sample #7, which was sent as an improvement of Sample #1, does show increased gasoline resistivity over Sample #1. However, it still has a gasoline solubility of an order which will permit the introduction of questionable amounts of gum into gasolines brought in contact with it.

15. Except for Sample #2, the spongy specimen, none of the materials show special promise as self-sealing agents of the type earlier discussed. The degree of swelling of these materials in the presence of gasoline is too slight to insure the closure of holes larger than microscopic. Sample #2 if used for a liner in a tank might, by virtue of its spongy structure, retard the escape of fluid through slit-like holes, but it probably would not be effective in the case of round or irregular punctures from bullets. Moreover, this particular specimen displays a high solubility even in paraffinic base stocks which militates against the use of it freely exposed to gasoline. Also, the prolonged action of gasoline gradually causes the spongy structure to become more compact and induces considerable shrinkage of the material.

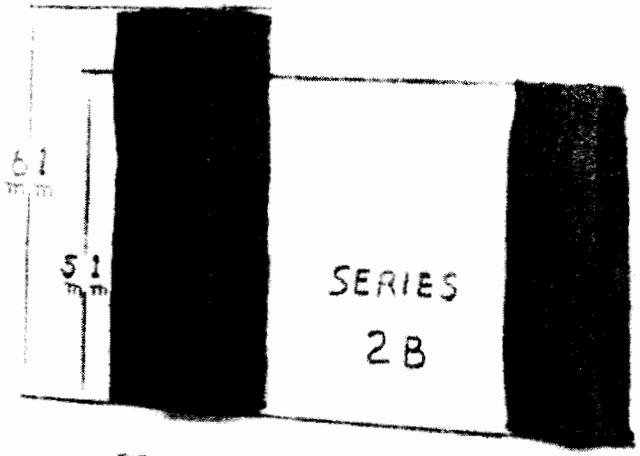
RECOMMENDATIONS

16. (1) From the samples studied, only specimens 4, 5 and 6 can be recommended for use in situations where prolonged contact with gasoline is necessary. The other samples are sufficiently soluble in gasoline to introduce amounts of gum exceeding the specification limits of 6 milligrams per 100 cc.

17. (2) Rubber or rubber-like substances should never be employed as protective liners for gasoline tanks or in the role of self-sealing agents unless the solubility of these materials in types of gasoline likely to be encountered is sufficiently low to exclude the contamination of fuel with dangerous amounts of gasoline soluble, gummy material.

[redacted]

EFFECT OF GASOLINE ON RUBBER [illegible]



ORIGINAL, UNTREATED

CONTACTED 30 DAYS

[redacted]

UNITED STATES RUBBER COMPANY

6600 East Jefferson Avenue

Detroit, Mich.

AUTOMOTIVE DIVISION

February 22, 1940

Naval Research Laboratory
Anacostia Station
Washington, D. C.

Attention: Mr. Parry Borgstrom.

Gentlemen:

Confirming our conversation with Mr. J. E. Sullivan of the Bureau of Aeronautics and Mr. Parry Borgstrom on February 14, you will find enclosed the following experimental samples of material upon which we would appreciate receiving your test findings:

Compound	5944-30-C
"	XM5999F1
"	61XM27
"	61XM294580
"	61XM284580
"	HVN-100

We would particularly appreciate your checking the sample HVN-100 in both of the two types of gasoline you use.

Mr. Borgstrom advised that strips of this type would be tested at 150° F. in a container which would contain both water and aviation gasoline.

We should very much appreciate learning from you the complete details of just how you conduct your test, so that we can duplicate this in our own laboratories and avoid sending you samples of material that have not already proven reasonably satisfactory in our own test.

Are the two types of gasoline which Mr. Borgstrom mentioned available on the open market? If so, we would like to know what we should ask for in order to procure exactly the same material you use for your test purposes.

Yours very truly,

/s/ W. R. YAW
Special Representative

WRY/h
cc - Chief of the Bureau of Aeronautics
Navy Department, Washington, D. C.

[redacted]

UNITED STATES RUBBER COMPANY

6600 East Jefferson Avenue

Detroit, Mich.

AUTOMOTIVE DIVISION

March 6, 1940

Naval Research Laboratories
Anacostia Station
Washington, D. C.

Attention: Mr. Parry Borgstrom

Gentlemen:

In the absence of Mr. W. R. Yaw, our Special Representative, and in reference to our conversation with Mr. J. E. Sullivan, of the Bureau of Aeronautics, and also in continuation of our letter of February 22, 1940, I am sending you attached a sample of our compound #5945-E for your test. This compound represents an improvement over the previous sample #5944-30-C.

Yours very truly,

/s/ E. EGER

EE:re

cc - Chief of Bureau of Aeronautics
Navy Department, Washington, D. C.

[redacted]