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TECHNICAL REPORT
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INITIAL COMPOUNDING STUDIES OF POLYPHOSPHAZENE RUBBER

by

Angus Wilson

August 1969

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

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FOREWORD

This is a report of results obtained from research compounding studies on small samples of polyphosphazene - a new elastomeric material. The rubber was produced by Horizons, Inc., under contract to the U. S. Army Materials and Mechanics Research Center, Watertown, Mass. The Rubber Technology Group at the U. S. Army Natick Laboratories carried out the compounding to evaluate the basic physical properties of the material and to determine the type of compounds obtainable from it, with a view toward satisfying the Army's need for a fuel-resistant rubber flexible at low temperatures. The work was performed under Project 1T062105A329, Organic Materials Research for Army Materiel.

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ABSTRACT

Polyphosphazene rubber, a new elastomeric material, was compounded with various curing agents and evaluated for fuel resistance, low temperature flexibility and general physical properties. The compounding studies showed that the polymer is curable with dicumyl peroxide in the presence of magnesium oxide. Testing showed that the polyphosphazene is a nonflammable material with an excellent combination of fuel resistance and low temperature properties. Its physical strength is weak but future polymerization work and improved compounding techniques may produce desired strength and provide a material suitable for use in Army applications.

INITIAL COMPOUNDING STUDIES OF POLYPHOSPHAZENE RUBBER

1. Introduction

Through the last two decades the U. S. Army has had a continuing interest in the development of a rubber with fuel resistance, good physical strength, and low temperature flexibility down to -50° to -65°F. Such a rubber is a necessity if the Army is to have an operational capability on a global scale. Many rubbers, obtained from commercial laboratories or developed under Government contract, have been compounded and evaluated, but to date none has had the desired combination of properties.

Recently, Horizons, Inc., under contract to the U. S. Army Materials and Mechanics Research Center, Watertown, Mass., synthesized new elastomeric polyphosphazenes. The materials were believed to have potential fuel resistance and low temperature flexibility, and samples were sent to the U. S. Army Natick Laboratories (NLABS) for research compounding and testing. The amounts received, while small, were sufficient for evaluation of the material's potential.

2. Materials

Two samples, numbered 1379-30 and 1408-12, were received with the following reported structure:

$$-\!\!\left[NP(OCH_2CF_3)_2 - NP(OCH_2C_3F_7)_2 \right]_x\!\!-$$

No. 1379-30 was a grey-tan gum, slightly tacky to the touch but separable from itself when pressed together. It possessed cold flow similar to that of raw butyl or silicone rubbers, and lost shape and definition on standing. Approximately 5 grams were received.

No. 1408-12, a white elastic gum, appeared to be a tougher material than No. 1379-30 with some resistance to tearing and rupture when hand-stretched. It was softer, however, than the majority of commercial gum elastomers and exhibited no apparent cold flow on standing. Approximately 13 grams were received. The two samples were received and evaluated separately.

3. Compounding and Testing of Sample No. 1379-30

Compounding and Molding - Because of the small amount of material available (5 grams), only three compounds were compounded and molded. A specimen of the uncompounded raw gum was also molded. The

0.75 gram of polymer used for each recipe was not sufficient to permit banding around the roll of a 3-inch mill, the smallest available for compounding. Ingredients were milled in by repeatedly removing the rubber from the mill roll, sprinkling the materials on the rubber surface, rolling the sheet up and passing it through the rolls. The compounding recipes used are shown in Table I.

TABLE I

COMPOUNDING RECIPES, SAMPLE 1379-30
(Parts per hundred parts of rubber by weight)

Compound	A	B	C
Polymer	100	100	100
Benzoyl Peroxide	1.5	---	---
Triethylenetetramine	---	1.5	---
Hexamethylenediamine Carbamate	---	2.5	---
Dicup 40C*	---	---	4
Zinc Oxide	5	5	---
Magnesium Oxide	---	---	5
Hisil 233**	15	15	15
Press Cure, Min/°F	60/240	60/250	60/290
Oven Post Cure, Hrs/°F	16/250	16/212	1.5/290 1.5/212 1.5/235 1.5/260 16/285

---

* 40% dicumyl peroxide supported on calcium carbonate
** Precipitated hydrated silica reinforcing fillers

The compounded material was molded and cured using a laboratory hydraulic press and a preheated mold with a 0.010-inch Teflon sheet on each side of the cavity plate. The press heat was turned off after curing and cooling water was turned on. Pressure was released when the mold had cooled to approximately room temperature.

To conserve material, the compounds were molded in the shape of the specimens used for testing. These specimens were 1-1/2 inches long, with a narrow straight portion 1 inch long and 0.125 inch wide with 0.25 inch square tabs at each end.

Compound Appearance - After press cure, Compound A was firm, smooth, free of bubbles and appeared to be vulcanized, although the molding flash of excess material gave evidence of weak tensile strength when it was hand-stretched and broken. Oven post-cure caused bubbling and the material became somewhat cellular.

Compound B bubbled during press cure and gave a weak, porous putty-like product with little evidence of cross-linking. There was no evident improvement after oven post-cure and the material was not evaluated.

Compound C, after press cure, was firm, smooth, bubble-free and apparently cross-linked, although of low tensile strength. Stepwise, oven post-cure did not cause porosity or bubbling.

<u>Test Procedures Used in Evaluation</u> - Torsional stiffness was run according to the "Procedure for Stiffness Measurements in Liquid Media" in ASTM Method D1053, but with air cooling by passage through dry ice as the medium.

Twist recovery was run according to a procedure developed at NLABS.(1)

Tensile strength and ultimate elongation tests were run using an Instron tester at a speed of 20 inches per minute. Elongation results are approximate since they are based on jaw separation distances.

Durometer hardness was run according to ASTM Method D-2240.

Weight loss was determined by placing approximately 0.4 gram of gum polymer in a tared aluminum pan and weighing on an analytical balance. The pan and specimen were heated in an oven for various times at increasing temperatures. After heating they were cooled in a desiccator and re-weighed.

Percent volume swell was determined according to ASTM Method D471.

Specific gravity was calculated from the values for specimen weights obtained in air and water in the volume swell test.

Flammability was evaluated by holding a small amount of material in a laboratory burner and observing burning characteristics.

<u>Test Results</u> (Table II) - The testing of the uncompounded gum showed the polyphosphazene to be a fuel-resistant and nonflammable polymer with low temperature flexibility to approximately -55°F. The material swells in acetone but is extremely fuel-resistant, as evidenced by the 9.8% swell in isooctane/toluene test fluid. Weight loss figures indicate good heat stability to 350°F.

Dicumyl peroxide (Compound C) produced the be[illegible]ure of the three agents tried, but even this gave a low tensile strength compared with those of commercial elastomers commonly available, and too low to provide the kind of strength needed in most Army end items. Benzoyl peroxide (Compound A) did not produce a compound suitable for tensile testing, and the attempted amine cure (Compound B) was unsuccessful. The good low temperature properties of the compounded materials were equivalent to those of the raw gum.

TABLE II

TEST RESULTS - SAMPLE 1379-30

Torsional Stiffness		Gum Polymer	Compound A	Compound C
°C	T_2	-32 (approx)	-38	-42
	T_5	-47.5	-45.5	-50
	T_{10}	-50.5	-48.5	-54
	T_{100}	-57.5	-61.5	-68
°F	T_2	-25.5	-36.5	-43.5
	T_5	-53.5	-50	-58
	T_{10}	-59	-55	-65
	T_{100}	-71.5	-78.5	-90.5
Twist Recovery				
°C	R_{180}	---	-17.5	-31.5
	R_{90}	---	-43.5	-44
	$R_{67.5}$	---	-45.5	-46.5
	R_{45}	---	-48	-48.5
	R_5	---	-56	-57
°F	R_{180}	---	+ 0.5	-24.5
	R_{90}	---	-46.5	-47
	$R_{67.5}$	---	-50	-51.5
	R_{45}	---	-54.5	-55.5
	R_5	---	-69	-70.5
Weight Loss, %				
4 hrs/212°F		0.26	---	---
2.5 hrs/250°F		0.49	---	---
2 hrs/300°F		0.99	---	---
2 hrs/350°F		1.83	---	---
2 hrs/518°F		16.88	---	---

TABLE II (Cont'd)

TEST RESULTS - SAMPLE 1379-30

Volume Swell, %	Gum Polymer	Compound A	Compound C
70/30 Isooctane/	9.8	---	---
Toluene Acetone	No result, excessive flow	96	43
Flammability	Vaporization & melting, no ignition	---	---
Tensile, psi	---	---	266
Elong, Ult, %	---	---	210
Hardness, Shore A Duro	---	---	55
Specific Gravity	1.736	1.474*	1.804

---

* Apparent gravity; lower than would be expected; caused by porosity

4. Compounding and Testing of Sample No. 1408-12

Since the tensile properties of Sample No. 1379-30 were low, compounding of 1408-12 was directed toward the investigation of various compounding combinations which might result in an improvement in physical properties.

Compounds and Results - The milling and molding procedures used for Sample No. 1379-30 were repeated. Initially, a test specimen of the same size and configuration was also used, but this was later changed, as described below, to provide a more accurate tensile strength measurement. The tensile and elongation measurements were again made with an Instron tester, and initial measurements (samples through 4C, Table III) employed an air-driven clamp instead of the mechanically tightened type previously used.

Since dicumyl peroxide had given the best cure with the previous sample, a series using this curing agent was prepared (Table III).

TABLE III

DICUMYL PEROXIDE COMPOUNDS - SAMPLE 1408-12

	Compound Number				
Compound Ingredients	X	1C	2C	3C	4C
Polymer	100	100	100	100	100
Dicup 40C*	---	4	2.5	2.5	3.5
MgO	---	5	---	---	---
Hisil 233**	---	15	40	---	---
HAF Black	---	---	---	---	20
Press Cure, Mins/°F	10/300	60/290	15/300	15/300	30/300
Oven Cure, Hrs/°F	---	1/190	.5/250	.5/200	.5/200
	---	1/212	16/300	16/300	.5/250
	---	1/250	---	---	16/300
	---	16/285	---	---	---
Compound appearance	Smooth, Soft	Smooth, free of bubbles	Smooth, hard & boardy	Soft, flowed badly during oven cure	Soft, tacky, bubbled
Tensile, psi	368	380	Collapsed in clamp	---	51

---

* 40% dicumyl peroxide supported on calcium carbonate
** Precipitated hydrated silica reinforcing fillers

The results showed the 1408-12 polymer to be stronger than the 1379-30 material. Dicumyl peroxide cures gave a tensile strength of 380 psi for the former and 266 psi for the latter. There was an indication that proper cure with the dicumyl peroxide requires the presence of an oxide such as MgO. (Note the difference between the tensile properties of Compound 1C with MgO and those of Compounds 2C, 3C and 4C without).

It soon became apparent that the air-clamping procedure used with the Instron tester on these specimens was not satisfactory since the specimens broke at the clamp edge instead of within their narrow section. Clamps were then fashioned from tubing clamps in which the upper clamping members were replaced with free-riding bars which increased grip as force was applied (Fig. 1). At the same time the size and configuration of the test specimen mold was changed to the dimensions shown in Figure 2. This change eliminated the sharp right-angled junctures where the tabs joined

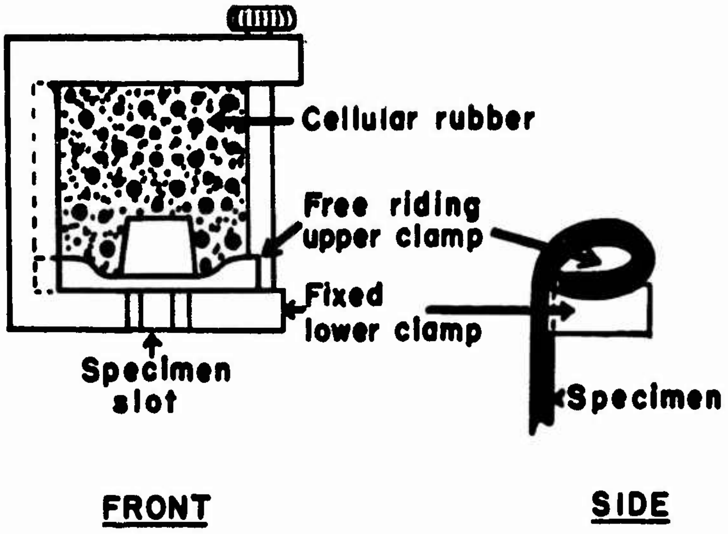

Figure 1 - Clamp

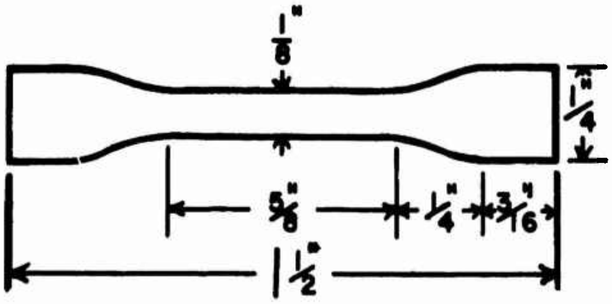

Figure 2 - Specimen

the narrow portion of the specimens, and which could well have served as tear loci, resulting in artificially low tensile values. Compound 1C was remade and tested using these clamps and the new mold. A tensile strength of 433 psi was obtained as compared with the previous 380 psi. The clamps and mold were used for the remainder of the testing.

Heat treatment during compounding is known to improve the physical properties of some polymers and Compound 1C was retested, but oven-heated one hour at 300°F after addition of the filler and oxide and prior to addition of the peroxide. The results are shown in Table IV under Compound 1C (A).

Another method used for improving physical properties (especially of silicone rubber) is bin aging, in which the rubber is compounded without a curing agent and allowed to age at room temperature for two weeks. It is then remilled, the curing agent added, and cured. This was done with Compound 5C (Table IV).

The curing effects of other peroxy materials were evaluated in Compounds 6C, 7C, 8C, and 11C (Table IV).

TABLE IV

VARIOUS PEROXIDE COMPOUNDS - SAMPLE 1408-12

Compound	Compound Number						
Ingredients	1C	1C (A)	5C	6C	7C	8C	11C
Polymer	100	100	100	100	100	100	100
Dicup 40C*	4	4	4	---	---	---	---
Cadox TS50**	---	---	---	1.5	1.5	---	---
Luperco 130XL***	---	---	---	---	---	1.5	---
Benzoyl peroxide	---	---	---	---	---	---	1.0
MgO	5	5	5	---	5	5	5
Hisil 233****	15	15	15	15	15	15	15
Heat treatment	---	1 Hr/300°F	---	---	---	---	---
Bin aging	---	---	2 wks	---	---	---	2 wks
Oven Cure, Mins/°F	60/290	60/290	60/290	15/240	15/240	15/300	60/250
Press Cure, Hrs/°F	1/190	1/190	1/190	1/190	1/190	1/190	1/190
	1/212	1/212	1/212	1/212	1/212	1/212	1/212
	1/250	1/250	1/250	1/250	1/250	1/250	1/250
	16/285	16/285	19/285	16/285	24/285	24/285	17/285
Tensile, psi	433	469	594	weak & cheesy	285	283	175
Approx. Ult elongation	230	280	200		270	220	190

---

* 40% dicumyl peroxide supported on calcium carbonate

** 50% 2,4 dichlorobenzoyl peroxide in silicone fluid

*** 50% 2,5 dimethyl 2,5 (t - butyl peroxy) hexyne - 3

**** Precipitated hydrated silica reinforcing fillers

The test results showed that dicumyl peroxide alone of the curin agents gave a cure with a tensile strength higher than the 368 psi previously obtained on the uncured polymer. Heat treatment of the dicumyl peroxide compound resulted in a slight increase in strength and two weeks bin aging resulted in a noticeable improvement - approximately 37% tensile increase.

The necessity of using an oxide in conjunction with a peroxide cure was again demonstrated in Compounds 6C and 7C - Compound 6C without an oxide being cheesy and too weak to permit testing. This peroxide/oxide dependency is known to exist in some fluorocarbon elastomers, such as the vinylidene fluoride-chlorotrifluoroethylene copolymers, in which good benzoyl peroxide cures were not obtainable without the incorporation of an oxide. The same behavior is shown by the polyphosphazenes.

Blends and Results - Commercially available elastomers, such as Fluorel and Viton, have sufficient fuel resistance and physical strength for Army end items but poor low temperature flexibility. It seemed possible that the use of small amounts of such materials as reinforcers for the polyphosphazene might improve its strength without jeopardizing its low temperature usefulness. Two compounds, 9C and 10C, were prepared using Fluorocarbon 214, a 70/30 copolymer of vinylidene fluoride and perfluoropropene, and a forerunner of Fluorel, developed approximately 10 years ago under an Army contract, which with a peroxide cure has a tensile strength of about 2800 psi. The recipes used and the results obtained are given in Table V.

Another blend investigated was that of the polyphosphazene with natural rubber. The fuel resistance of the phosphazene by itself, characterized by its 10% swell in isooctane/toluene test fluid, is better than that actually required in some Army applications where 30 to 40% might be satisfactory. It was theorized that the use of natural rubber with its attractive physical and low temperature properties could result in a blend which retained these good properties, with some sacrifice in fuel resistance. Such a blend was formulated in Compound 12C. The recipe and results are given in Table V.

TABLE V

PHOSPHAZENE BLENDS - SAMPLE 1408-12

	Compound Number			
Compound Ingredients	9C	10C	11C	12C
Phosphazene 1408-12	80	70	100	75
Fluorocarbon 214	20	30	---	--
Natural pale crepe	--	--	---	25
Hisil 233	15	15	15	20
MgO	5	5	5	5

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TABLE V (Cont'd)

PHOSPHAZENE BLENDS - SAMPLE 1408-12

	Compound Number			
Compound Ingredients	9C	10C	11C	12C
Bin aged	2 wks	2 wks	2 wks	---
Dicup 40C	4	4	---	4
Benzoyl peroxide	---	---	1	---
Press Cure, Mins/°F	60/290	60/290	60/250	60/290
Oven Cure, Hrs/°F	1/190	1/190	1/190	1/175
	1/212	1/212	1/212	1/212
	1/250	1/250	1/250	1/250
	17/285	17/285	17/285	16/285
Tensile, psi	380	444	175	Smooth, flexible specimen after press cure, but stiff and boardy after oven cure, broke on bending
Volume swell, % 24 hrs, 70/30 isooctane/toluene	7	7	11	
Torsional Stiffness				
°C T_2	-16	-16	-38	---
T_5	-31	-21.5	-45	---
T_{10}	-42.5	-24	-51	---
T_{100}	-56	-53.5	-62	---
°F T_2	+ 3	+ 3	-36.5	---
T_5	-24	- 6.5	-49	---
T_{10}	-44.5	-11	-60	---
T_{100}	-69	-64	-80	---
Specific Gravity	1.81	1.82	1.78	---

None of the blends achieved the desired results. The addition of the fluoroelastomer, for example, severely hindered the low temperature flexibility of the phosphazene, as evidenced by the change in the T_5 values, without giving the desired improvement in tensile strength. The fuel resistance remained virtually unchanged as would be expected. The natural rubber blend had very little resistance to heat aging and embrittled during oven cure.

5. Discussion

This study of the compounding of polyphosphazene rubber demonstrated the excellent combination of fuel resistance and low temperature flexibility of the material. The combination is the best to date of any fluorine-containing elastomer developed under the long-term Army rubber research effort. Fuel resistance is equivalent to that of nitroso rubber copolymer while low temperature flexibility, as shown by the torsional stiffness T_5 value, is approximately 27°F lower.(2)

The nonflammability of the polyphosphazene also makes it additionally attractive for Army item use. The drawback most apparent at this time is its low tensile strength, approximately 600 psi, which should be increased about threefold to provide needed toughness. It is assumed that good abrasion resistance and tear strength will accompany good tensile strength, or that they at least will be obtainable. The compounding techniques and specimen size were not conducive to the development of optimum physical properties. However, it is apparent that the material tested so far is weak. Whether this is inherent, as it is with silicone rubber, for example, or whether it can be improved by changes in polymerization, or by compounding, remains to be determined in future work.

The compounds tested show that dicumyl peroxide in the presence of MgO cures the material. The efficacy of the other peroxides used is questionable, but does not preclude good cures being obtained with them. Benzoyl peroxide is notably sensitive to impurities and the presence of other chemicals in the compound. The right combination of ingredients in a compound may result in an improvement in benzoyl peroxide curing, but this again will depend on future research compounding.

6. Recommendations

It is recommended that compounding studies on polyphosphazene be continued with a view toward:

a. Improving tensile strength and other physical properties,

b. Determining the combinations of materials which will provide an optimum curing system,

c. Evaluating properties of the resulting compounds with regard to their possible applications to Army end items.

7. References

1. Wilson, A., Measurement of Rubber Elasticity at Low Temperatures Using a Twist Recovery Apparatus, U. S. Army Natick Laboratories Technical Report 66-4-CM, (C&OM-14), January 1966.

2. Griffis, C. B. and M. C. Henry, Nitroso Rubbers, Rubber and Plastics Age, 46, No. 1, 63 (1965).

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13. ABSTRACT

Polyphosphazene rubber, a new elastomeric material, was compounded with various curing agents and evaluated for fuel resistance, low temperature flexibility and general physical properties. The compounding studies showed that the polymer is curable with dicumyl peroxide in the presence of magnesium oxide. Testing showed that the polyphosphazene is a nonflammable material with an excellent combination of fuel resistance and low temperature properties. Its physical strength is weak but future polymerization work and improved compounding techniques may produce desired strength and provide a material suitable for use in Army applications.

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	ROLE	WT	ROLE	WT	ROLE	WT
Compounding	8					
Polyphosphazene rubber	1,2		9			
Curing agents	1					
Fuel resistance	4		8			
Low temperature tests	4		8			
Flexibility	4		8			
Physical properties	4		8			