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POLY(PHOSPHAZENE) WIRE AND CABLE INSULATION.(U)
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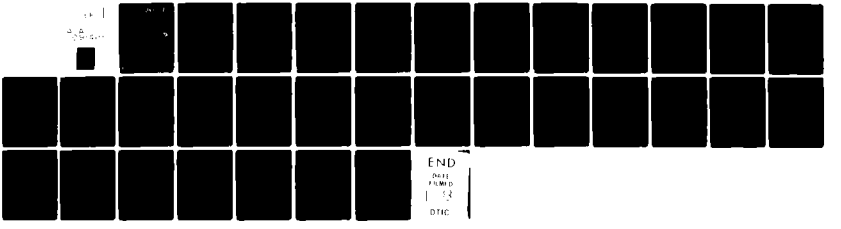

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(6) POLY(PHOSPHAZENE) WIRE AND CABLE INSULATION

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by

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POLY(PHOSPHAZENE) WIRE AND CABLE INSULATION

1.0 OBJECTIVE

The objective of the program under Contract No. N00024-78-C-4644 is to prepare a fire resistant cable utilizing a single poly(aryloxyphosphazene) (Firestone APN®) base material for both the wire insulation and the cable jacket. Formulations will be developed which offer maximum fire retardancy and low smoke generation while achieving optimum electrical properties for the wire insulation and optimum physical properties for the jacketing.

Four APN® polymers will be prepared to evaluate molecular weight and compositional effects on properties and processing. The single best candidate will be pilot plant produced by The Firestone Tire & Rubber Company (Akron, Ohio) and cabled product will be prepared by Boston Insulated Wire and Cable Company (Boston, Massachusetts). One very low molecular weight APN® polymer will be prepared and be evaluated as a flame-retardant plasticizer.

2.0 SUMMARY

Five poly(phenoxy-4-ethylphenoxyphosphazene) (APN®) copolymers were prepared. Three of these polymers met target viscosities and were used to evaluate the effects of molecular weight and composition on properties and processing. A sixth, very low molecular weight copolymer was evaluated as a reactive fire-retardant plasticizer.

Little or no effect of polymer structure on properties or processing has been observed. A change of 14 percentage points in the substituent ratio had no effect on the value for NBS smoke density. High molecular weight material afforded marginally better physical properties than low molecular weight material. Low molecular weight polymeric plasticizer reduced Limiting Oxygen Index (LOI) by 4 units.

By proper filler selection, physical properties easily surpassed specifications. Tensile strengths of 900 psi at elongations of 180% were obtained routinely. Electrical properties, dielectric constant and dissipation factor, are slightly higher than specification; whereas, dielectric strength is at least double that of specification. Excellent fire retardancy and low smoke generation are coupled with these properties.

Good retention of physical properties was obtained in isothermal aging studies at 125°C after 312 hours.

Use of several smoke suppressant synergists had an adverse effect on physical properties when tested.

A 200 pound batch of pilot plant produced APN® polymer supplied by The Firestone Tire & Rubber Company was found to be suitable for use in cable fabrication when upgraded.

The requirements of the cable fabricator's equipment necessitated some formulation changes that resulted in some loss in physical properties (elongation). The new formulations will still meet specifications for physical properties.

The final formulations could be mixed on normal production type rubber mills. Mixes were 130 pounds each. The properties of the large scale mixes were not as good as those of small scale mixes.

3.0 DISCUSSION AND RESULTS

3.1 Synthesis

Four high molecular weight poly(phenoxy-4-ethylphenoxyphosphazene)(APN®) copolymers and one very low molecular weight APN® copolymer were prepared by the two-step chemistry shown in Equations (1) and (2).

$$\underset{\text{(monomer)}}{(NPCl_2)_3} \xrightarrow[\text{catalyst}]{\Delta} \underset{\text{(polydichlorophosphazene)}}{[NPCl_2]_n} \qquad (1)$$

$$[NPCl_2]_n + NaOC_6H_5 + NaOC_6H_4\text{-}C_2H_5 \xrightarrow{\Delta} [(C_6H_5O)(4\text{-}C_2H_5C_6H_4O)PN]_n \qquad (2)$$

(APN®)

In order to obtain APN® copolymers of high molecular weight, poly(dichlorophosphazene) of high molecular weight had to be prepared. Polymerization studies of $(NPCl_2)_3$ monomer were conducted in the presence of catalyst using 1,2,4-trichlorobenzene solvent. Polyphosphoric acid, phosphorus pentoxide, and mixtures thereof were employed as catalysts at solution temperatures of 200-205°C.

Two problems were encountered in the preparative effort. One related to scale up and one related to polymer viscosity.

The scale up problem was that extremely low polymerization rates occurred on a 3 kg monomer scale in comparison to a 200 g monomer scale. Polymerization of 3 kg monomer was necessary to yield 1 kg of $[NPCl_2]_n$ polymer which in turn would be converted to at least 1 kg of APN® copolymer. The scale up phenomenon was largely attributed to inadequate stirring of the heterogeneous system. Fortunately, polymerizations at 1.5 kg monomer scale in a 3 liter reaction flask closely approximated small scale runs.

Conversion of poly(dichlorophosphazene) to APN® copolymers was conducted by reacting $[NPCl_2]_n$ with a diglyme solution of sodium phenoxide and sodium 4-ethylphenoxide at 125-127°C for at least 48 hours. The mole ratio of aryloxide salts was varied from 50:50 to 35:65 in order to introduce compositional effects at a similar molecular weight level. This was accomplished by equally dividing a solution of $[NPCl_2]_n$ polymer and reacting one-half with the 50:50 reactant mixture and the other half with the 35:65 reactant mixture. Four candidate APN® copolymers resulted from performing this process at two molecular weight levels of $[NPCl_2]_n$ polymer.

Unexpectedly, initial polymer viscosities were considerably higher than target values. This necessitated lowering polymer viscosities. In two instances (polymers 1 and 2) this was achieved by heating a xylene-diglyme solution of polymer (partially purified) at about 130°C for several hours. In the other two cases (polymers 3 and 4) viscosity (or molecular weight) was lowered by post-heating the original reaction mixture containing aryloxide salts for 6-7 hours at 150°C.

All polymers were isolated by precipitation with methanol followed by washing and vacuum drying. Purified APN® polymers were obtained in high yields. The polymers were characterized by dilute solution viscosity, elemental analysis, and Nuclear Magnetic Resonance (NMR) spectroscopy. Very low chloride content was found in all instances. This is important in achieving optimum electrical and stability properties.

When polymers 3 and 4 were completely characterized, there was surprisingly a large discrepancy in viscosity values from preliminary (1.6 and 1.6 dl/g) and final (1.15 and 1.25 dl/g) samples. The target viscosity value was 1.6 dl/g. This necessitated the preparation of another polymer, No. 5, with high viscosity value. A comparison high molecular weight polymer with different $C_6H_5O/4\text{-}C_2H_5C_6H_4O$ ratio was not prepared because compositional effects on vulcanizate properties of the lower molecular weight set were not evident. It was felt that better use of time would be made by pursuing optimization of wire and cable formulations. The high molecular weight polymers were characterized as shown in Table I. The low molecular weight APN® plasticizer (0.5 kg) was of molasses-like consistency with a viscosity of 0.2 dl/g.

TABLE I

CHARACTERIZATION OF $[(C_6H_5O)(4\text{-}C_2H_5C_6H_4O)PN]_n$ (APN®) COPOLYMERS

Polymer No.	Yield, % (kg)	Intrinsic Viscosity, dl/g (benzene, 30°C) (target value)	$C_6H_5O/4\text{-}C_2H_5C_6H_4O$ Ratio (by NMR) (target value)	% Cl [(a)]
1. 2556-06	93 (1.2)	1.1 (1.1)	59.3:40.7 (50:50)	0.087
2. 2556-08	93 (1.2)	1.0 (1.1)	45.6:54.4 (35:65)	0.059
3. 2556-12	90 (1.1)	1.15 (1.6)	51.3:48.7 (50:50)	0.08
4. 2556-16	90 (1.2)	1.25 (1.6)	34.3:65.7 (35:65)	0.09
5. 2556-30	82 (0.83)	1.75 (1.6)	41.5:58.5 (35:65)	0.06

(a) Negative Beilstein test obtained for all samples. This is a very sensitive qualitative test to determine the presence of chlorine.

3.2 Compounding and Testing Studies

All polymers handled easily on standard rubber compounding equipment (i.e. Brabender internal mixer and 2-roll mill) when a silicone processing aid was used to eliminate mill stick. The initial formulation followed a wire covering recipe previously developed at Horizons [Ref. 1] for a very high molecular weight APN® material. As anticipated from the earlier effort at Horizons, physico-mechanical properties of poly(phosphazene) vulcanizates are highly dependent on filler loading, curative, curing conditions and gum polymer. Target physical, electrical, flame spread, and smoke properties are shown in Table II.

TABLE II

TARGET PROPERTIES OF POLY(PHOSPHAZENE) WIRE AND CABLE COVERING MATERIAL

Property	Requirement
Tensile strength, psi (min.)	800
Elongation, % (min.)	100
Dielectric strength, volts/mil (min.)	300
Dielectric constant (100 KHz) (max.)	4.5
Dissipation factor (100 KHz) (max.)	0.02
NBS smoke density (max.) (20-25 mil sample)	100 (flaming) 100 (nonflaming)
Flame Spread Index	25

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1. K. A. Reynard and J. C. Vicic, "Polyphosphazene Wire Coverings," Horizons Incorporated, Final Technical Report to Naval Ship Engineering Center, Contract N00024-75-C-4402, June 1976.

A cure temperature of 177°C (350°F) was selected on the basis of Monsanto oscillating disc rheometer studies. Limiting Oxygen Index (LOI) was selected as the property to compare relative fire retardancy. Results of these studies are shown in Table III. The low tensile values are attributed to the relatively low molecular weight of the APN® polymers. Tensile values of 900-1000 psi were reported previously [Ref. 1] using APN® polymer with viscosity values of 2.0-2.2 dl/g. These very high molecular weight materials were much more difficult to process. Current materials afforded acceptable elongation and LOI values.

3.2.1 Filler Studies

The greatest effects on physical properties result with changes in filler type and loading as seen in Table IV. The data in Table IV clearly show that use of Hydral 705 affords the highest tensile values whereas Lubral Hydral 710 easily affords the highest elongation values. Magnesium carbonate ($MgCO_3$) was evaluated as a supplemental filler because magnesium is believed to have a synergistic effect with alumina hydrate in lowering smoke. In addition, the neutral character of $MgCO_3$ could afford better electrical properties when compared to the highly basic magnesium hydroxide, $Mg(OH)_2$.

Other filler studies showed that Hi-Sil did not improve physical properties nor did Solem 632-SP improve electrical properties. These findings are contrary to earlier work [Ref. 1]. Catapal SB alumina, an alumina monohydrate, gave inferior properties when used as replacement for Solem 632-SP. The Catapal material was studied because it might act as internal drying agent which could improve electrical properties.

Optimized wire and cable covering formulations with resultant properties are shown in Tables V and VI.

3.2.2 Polymer Studies

The effect of polymer structure (i.e. C_6H_5O/-4-$C_2H_5C_6H_4O$ substituent ratio) and polymer viscosity (i.e. molecular weight) on vulcanizate properties was determined using a jacketing formulation. The data in Table VII show that there were no experimental differences in tensile, elongation, hardness or LOI between low molecular weight polymers with 1:1 and 1:2 substituent mole ratios. For the

TABLE III

PRELIMINARY PHYSICAL PROPERTIES[a] OF POLY(PHOSPHAZENE) WIRE COVERING MATERIAL

Polymer No.	Properties			
	Tensile Strength, psi (desired 800 psi, min.)	Elongation, % (desired 100%, min.)	Shore A Hardness	LOI (desired 35 min.)
1	660	190	47	33
2	670	180	47	--
3	620	125	52	35

(a) Vulcanizates were prepared from 100 parts polymer, 25 parts magnesium hydroxide, 50 parts silane treated alumina trihydrate, 10 parts Silastic HA-2 (processing aid), and 1 part Vulcup 40KE (peroxide). Cure conditions: 7 minutes at 177°C.

TABLE IV

EFFECT OF FILLER ON POLY(ARYLOXYPHOSPHAZENE) VULCANIZATE PROPERTIES

Property	Filler (a)						
	Hydral 705		2% Lubral Hydral 710		Solem 632-SP		
	As is	with $MgCO_3$ (25 phr)	As is	with $MgCO_3$ (25 phr)	As is	Hi-Sil EP (20 phr)	Hi-Sil 233 (20 phr)
Tensile strength, (psi)	880	790	800	720	700	680	710
Elongation at Break (%)	150	135	275	185	215	145	130
Hardness, Shore A	44	52	38	48	43	54	59
Limiting Oxygen Index(b) (LOI)	35-1/2	34-1/2	32-1/2	32-1/2	34-1/2	36	36

(a) Formulation comprises 100 parts poly(aryloxyphosphazene), 50 phr filler, 25 phr $Mg(OH)_2$, 10 phr Silastic HA-2. Hydral fillers supplied by ALCOA are alumina trihydrates, the 705 grade has the lowest particle size and Lubral Hydral 710 has been treated with a proprietary fatty acid derivative (2%). Solem 632-SP is a silane treated alumina hydrate and the Hi-Sils are reinforcing silicas.

(b) Measure of flame-retardancy.

TABLE V

PROPERTIES OF POLY(PHOSPHAZENE) WIRE COVERING

	Property	Peroxide Level (parts) 1-1/4	1-1/2	2
Sample No. 2563-38	Tensile Strength, psi	860	880	940
100 Polymer (HMW) No.5 50 Lubral Hydral 25 $Mg(OH)_2$ 10 Silastic HA-2	Elongation at Break, %	280	260	195
	Hardness, Shore A	33	38	42
	LOI	29-1/2	31-1/2	32-1/2
	Dielectric Constant, 10 KHz	4.7	5.1	5.0
	100 KHz	4.2	4.9	4.7
	Dissipation Factor, 10 KHz	.017	.034	.032
	100 KHz	.022	.034	.031
	Dielectric Strength, volts/mil	710	---	---

		Peroxide Level (parts) 1	1-3/4
Sample No. 2563-42			
100 Polymer (HMW) No.5 50 Hydral 705 25 Mg(OH)2 10 Silastic HA-2	Tensile Strengths, psi	840	940
	Elongation at Break, %	280	190
	Hardness, Shore A	33	41
	LOI	31	33

TABLE V (Contd.)

Sample No. 2563-42 (contd.)		Peroxide Level (parts) 1	1-3/4
Dielectric Constant,	10 KHz	5.0	5.0
	100 KHz	5.0	5.0
Dissipation Factor,	10 KHz	.015	.019
	100 KHz	.025	.026
Dielectric Strength, volts/mil		610	795

TABLE VI

PROPERTIES OF POLY(PHOSPHAZENE) CABLE COVERING (JACKETING)

Property	Formulation A	Formulation B	Formulation C
	Peroxide Level (parts)		
	2	2	2 to 2-1/2
Tensile Strength, Psi	800	840	750 to 850
Elongation at Break, %	150	130	155 to 130
Hardness, Shore A	53	56	52 to 58
LOI	38-1/4	40	41 to 42
NBS Smoke Density, D_{mc} (flaming mode)	74	84	-- to --

(A) - Sample No. 2571-08A
100 Polymer (HMW) No. 5
90 Hydral 705
15 $Mg(OH)_2$
10 Silastic HA-2

(B) - Sample 2571-15
100 Polymer (HMW) No.5
70 Hydral 705
30 $Mg_3(PO_4)_2 \cdot 4H_2O$
5 $Mg(OH)_2$
10 Silastic HA-2

(C) - Sample 2571-05
100 Polymer (HMW) No.5
100 Hydral 705
5 $Mg(OH)_2$
10 Silastic HA-2

TABLE VII

EFFECT OF POLYMER STRUCTURE AND POLYMER MOLECULAR WEIGHT ON POLY(ARYLOXYPHOSPHAZENE) VULCANIZATE PROPERTIES

Formulation 2563-	13	17	22D	33B	39A	34A	42A	42B
Polymer(a)								
2556-08 (LMW, 1:2) No. 2	100	--	--	100	--	100	--	--
2556-06 (LMW, 1:1) No. 1	--	100	100	--	--	--	--	--
2556-30 (HMW, 1:2) No. 5	--	--	--	--	100	--	100	100
Solem 632 SP	50	50	50	--	--	--	--	--
2% Lubral Hydral 710	--	--	--	50	50	--	--	--
Hydral 705	--	--	--	--	--	50	50	50
$Mg(OH)_2$	25	25	25	25	25	25	25	25
Silastic HA-2	10	10	10	10	10	10	10	10
Peroxide:								
Vulcup 40KE	1	1	--	--	--	--	--	--
Luperco 500-40KE	--	--	1	1	1-1/2	1	1	1-3/4
Properties								
Tensile strength, psi	670	660	700	800	880	880	840	940
Elongation at break, %	180	190	215	275	260	150	280	190
Hardness, Shore A	47	47	43	38	38	44	33	41
LOI	--	33	34-1/2	32-1/2	31-1/2	35-1/2	31	33

(a) LMW = Low molecular weight, dilute solution viscosity = 1.1 dl/g.
HMW = High molecular weight, dilute solution viscosity = 2.1 dl/g.
1:1 and 1:2 Designate substituent mole ratios of $C_6H_5O/4\text{-}C_2H_5C_6H_4O$.

1:2 substituent ratio polymers there was little difference in physical properties between high and low viscosity polymers. The low viscosity polymer did have a better LOI value by nearly 4 units.

3.2.3 Curing Agent Studies

Vulcanizates were prepared by curing in a press at 350°F for 5-7 minutes using organic peroxides as cross-linking agent. The effect of curing agent on vulcanizate properties is shown in Table VIII. The low molecular weight 1:1 polymer was employed for these studies.

TABLE VIII

EFFECT OF PEROXIDE ON POLY(ARYLOXYPHOSPHAZENE) VULCANIZATE PROPERTIES

Properties	Luperco 500-40KE	Vulcup 40KE	USP 130 KXL	101-XL
phr peroxide	1	1	2	3/4
Tensile strength, psi	700	660	650	600
Elongation at break,%	215	190	195	210
Hardness, Shore A	43	47	43	41
LOI	34-1/2	33	32-1/2	33

Formulation: 100 polymer, 50 Solem 632-SP, 25 $Mg(OH)_2$, 10 Silastic HA-2.

Luperco 500-40KE proved to be best overall. Unfortunately Luperco vulcanizates have an irritating odor.

3.2.4 Comparison of Horizons and Firestone Polymers

A small amount of poly(aryloxyphosphazene) was obtained from Firestone for a comparative study. This study is very significant because the polymer to be used for wire and cable insulation will be prepared by Firestone. The results shown in Table IX were extremely favorable. The

TABLE IX

COMPARISON OF FIRESTONE AND HORIZONS POLY(ARYLOXYPHOSPHAZENES) ON VULCANIZATE PROPERTIES

Formulation	Cable Covering 2571-08A			Wire Covering 2563-38	
Polymer (HMW) No. 5	100			100	
Hydral 705	90			--	
2% Lubral Hydral 710	--			50	
$Mg(OH)_2$	15			25	
Silastic HA-2	10			10	
Property	**Polymer[a] Source**				
	F	F	H	F	H
Peroxide[b] level, phr	1.5	2.5	2	1.5	1.5
Tensile strength, psi	750	850	800	850	880
Elongation at break, %	325	200	150	390	260
Hardness, Shore A	50	55	53	32	38
Limiting Oxygen Index (LOI)	38	38-1/2	38-1/4	32-1/2	31-1/2
Dielectric constant: 10 KHz	4.9	4.6	5.1	4.9	5.1
100 KHz	4.8	4.45	5.0	4.8	4.9
Dissipation factor: 10 KHz	.017	.019	.020	.022	.034
100 KHz	.020	.053	.028	.021	.034

(a) Firestone polymer (F) has a dilute solution viscosity of 1.73 dl/g (benzene, 30°C) and a $C_6H_5O/4\text{-}C_2H_5C_6H_4O$ ratio of 53/47. Horizons polymer (H) has a dilute solution viscosity of 2.18 dl/g (benzene, 30°C) (or an intrinsic viscosity of 1.75 dl/g) and a $C_6H_5O/4\text{-}C_2H_5C_6H_4O$ ratio of 41.5/58.5.

(b) Luperco 500-40KE.

Firestone material equalled or surpassed the Horizons material in all properties tested.

3.2.5 Isothermal (125°C) Aging Studies

The dramatic effect of stabilizers on aging poly(aryloxyphosphazene) vulcanizates is clearly shown in Table X. Samples were aged isothermally in a circulating air oven at 125°C (257°F). Irganox 1010 is an antioxidant whereas zinc 8-hydroxyquinolate is a thermal stabilizer for poly(organophosphazenes). Optimization of stabilizer levels and/or use of co-stabilizers significantly improve heat aging properties. A concurrent study of heat aging on electrical properties was not performed.

3.2.6 Smoke Suppressant Synergists

Use of materials which act synergistically with a fire retardant often enhance fire retardancy and/or reduce smoke evoluation upon combustion. Three smoke suppressant synergists were evaluated as shown.

TABLE XI

EFFECT OF SMOKE SUPPRESSANT SYNERGISTS

	Control	FR-515	Firebrake ZB	$(NH_4)_2Mo_2O_7$
2% Lubral Hydral 710:Syn.	--	2:1	3:1	4:1
Tensile strength, psi	800	420	770	650
Elongation at break, %	275	155	240	210
Hardness, Shore A	38	36	41	37
LOI	32-1/2	29-1/2	31-1/2	31-1/2

FR-515 is a proprietary organic compound. It evolved a gas during cure that led to spongy stock. Firebrake ZB gave the smoothest surfaces being nearly bubble free. The three materials did not warrant smoke and further fire-retardancy evaluation because of their negative effects on physical and LOI properties.

TABLE X

EFFECT OF STABILIZERS ON AGING POLY(ARYLOXYPHOSPHAZENE) VULCANIZATES IN AIR AT 125°C (257°F)

Formulation	2571-08A			2571-17B				
Copolymers 2556-30, No. 5 (hi mol. wt. $C_6H_5O/4\text{-}C_2H_5C_6H_4O$ ratio of 1:2)	100			100				
Hydral 705	90			90				
$Mg(OH)_2$	15			15				
Silastic HA-2	10			10				
Luperco 500-40KE	2			3				
Irganox 1010				0.5				
Zinc 8-hydroxyquinolate				0.5				
	125°C Hours							
Property	0	72	144	0	72	144	240	312
Tensile strength, psi	800	1,060	--	830	980	990	1,040	990
Elongation, %	150	30	--	90	80	75	75	80
Hardness, Shore A	53	72	--	57	62	67	67	67

3.2.7 Effect of Composition on Smoke Generation

The two polymers for this study were prepared from the same chloropolymer. The substituent ratios were adjusted so that final polymer composition would be different but the polymers would be the same in all other respects. The cable covering formulation of Table IX was used for all comparisons. Table XII summarizes the properties of these polymers.

TABLE XII

PROPERTIES OF POLYMERS FOR SMOKE GENERATION STUDY

Polymer	No. 2	No. 1
Composition by NMR		
% Phenoxy	45.6	59.3
% Ethylphenoxy	54.4	40.7
Intrinsic Viscosity dl/g, benzene, 30°C	1.03	1.10
% Residual Chlorine	0.06	0.09
% Yield	93	93
Vulcanizate Properties		
Tensile strength, psi	690	700
Elongation at break, %	185	185
Hardness, Shore A	52	53

The polymers were similar in all respects except for the variation in substituent composition. Table XIII shows the flame properties of these two polymers in the same formulation used above.

TABLE XIII

EFFECT OF COMPOSITION ON FLAME PROPERTIES

Polymer	No. 2	No. 1
LOI	42	42
NBS Smoke Density (D_{mc})		
Smoldering	8	8
Flaming	69	75

Within experimental error, there were no differences in flame properties due to a change of 14 percentage points in substituent ratio.

3.2.8 Plasticizer Study

Four plasticizers were evaluated in the event there was a need for improving processability or elongation. Effects on physicals and LOI were determined at the 5 phr level. The results are shown in Table XIV.

TABLE XIV

EFFECT OF PLASTICIZER ON POLY(ARYLOXYPHOSPHAZENE) VULCANIZATE PROPERTIES

	Tensile Strength (psi)	Elongation at Break (%)	Hardness, Shore A	LOI
Control	680	145	54	36
DBEP	540	145	46	36
DOP	550	165	45	36
Cumar P-10	330	195	33	35
Low MW APN[(a)]/DOP (1:1)(5 phr)	600	145	47	35
Low MW APN[(a)]/DOP (1:1)(10 phr)	570	150	47	35

(a) Low molecular weight poly(aryloxyphosphazene), dilute solution viscosity = 0.8 dl/g (benzene, 30°C).

Kenflex A at the 5 phr level was evaluated as a plasticizer in the jacketing formulation 2571-08A. LOI fell by 1/2 unit with little change in other properties.

Low molecular weight poly(aryloxyphosphazene) polymeric plasticizer (dilute solution viscosity = 0.15 dl/g) at the 5 phr level reduced LOI by 4 units in wire covering formulation 2563-34.

3.3 Pilot Plant Produced Polymer

The Firestone Tire & Rubber Company prepared 200 pounds of APN® polymer. This pilot plant produced polymer was very different from the previous material supplied by Firestone described in Section 3.2.4 of this report. Table XV is a comparison of the first Firestone polymer with the second (200 pound batch) polymer.

TABLE XV

COMPARISON OF FIRESTONE POLYMERS

Formulation	Cable Covering				Wire Covering		
Polymer	100				100		
Hydral 705	90				--		
2% Lubral Hydral 710	--				50		
$Mg(OH)_2$	15				25		
Silastic HA-2	10				10		
Polymer	First	Second			First	Second	
Peroxide level, phr (Luperco 500-40KE)	2.5	2.5	3.5	4	1.5	1.5	2.5
Tensile strength,psi	850	600	710	780	850	660	850
Elongation at break,%	200	365	340	215	390	545	345
Hardness, Shore A	55	46	45	53	32	23	30

The second polymer had a larger fraction of low molecular weight polymer in it. This contributed to the lower tensiles and higher elongations observed in its vulcanizates. There also appeared to be a trace impurity present that interfered with the peroxide curing system. Attempts were made to achieve the specification values by compounding changes. As peroxide levels are increased, LOI values decrease due to the extra organics present. To add more peroxide with less organic material, Luperco 500-40KE was replaced by Vulcup 40KE. Vulcup 40KE is a diperoxide and 2-1/2 parts is equivalent to 4 parts of Luperco 500-40KE. Table XVI shows the effect of this substitution.

TABLE XVI

EFFECT OF INCREASED PEROXIDE LEVELS
ON SECOND POLYMER

	Cable Covering			Wire Covering
Peroxide Level, phr (Vulcup 40KE)	2.5	3	3.5	2.5
Tensile strength, psi	780	790	750	900
Elongation at break, %	235	185	155	285
Hardness, Shore A	53	56	60	35

From the above tables it can be seen that the wire covering formulation would exceed the minimum specifications of 800 psi and 100% (preferably 200-300%) elongation using the second polymer. It can also be seen this approach would not give the desired results with the cable covering formulation. Changes were then limited to the cable covering only for further development.

A one hour post cure at 350°F was tried but had little effect on tensile or elongation. Both values increased slightly (~ 3-5%). Shore A increased 5 units. A second approach was to use two peroxides; a low temperature peroxide to scavenge reactive impurities and the usual peroxide to cure. This resulted in greater elongations (200-300%) but no increase in tensiles (750-770 psi). The addition of stearic acid, zinc stearate, zinc chloride or zinc peroxide to the formulation at the 2 phr level gave no improvement.

Firestone personnel supplied two special samples derived from the second polymer. Sample A was dissolved in tetrahydrofuran and was precipitated with water. Sample B was dissolved, centrifuged and evaporated. Ten pounds of the polymer was treated as Sample A and is shown as Sample C in the following table.

TABLE XVII

EFFECT OF TREATED POLYMER ON PROPERTIES

Polymer	A			B			C
Peroxide Level, phr							
Luperco 500-40KE	2.5	3.5	2.5	2.5	3.5	2.5	3.5
Alperox F	--	--	1	--	--	1	--
Tensile strength, psi	760	*	850	780	930	850	880
Elongation at break, %	260	*	275	305	210	325	255
Hardness, Shore A	46	56	44	44	53	44	48

*Malfunction; insufficient polymer to repeat.

The upgraded polymer meets specifications for the cable covering formulation and should easily do so for the wire covering formulation.

Although the 200 pound batch of polymer did not initially meet specifications, by working with Firestone personnel, a way was found to upgrade the polymer. The upgraded polymer gave vulcanizates with tensile strengths equivalent to that of previous materials, better values for elongation but lower hardness values. The upgraded polymer was characterized as follows:

$C_6H_5O/4\text{-}C_2H_5C_6H_4O$ ratio by NMR	53.2/46.8
Chlorine content	0.04%
Dilute solution viscosity	1.38 dl/g

The residual chlorine content and viscosity were within limits specified by Horizons. The substituent composition was far from the requested 35/65 $\pm$ 5 mole %. The altered composition should have no effect on flame properties as demonstrated by Section 3.2.7 of this report. Physical properties of vulcanizates were within specifications or better. Since polymer delivery required 6 months and delivery time for another batch would be uncertain, the decision was made to accept the upgraded polymer and proceed with cable fabrication. This cable would have the same burning characteristics as one produced from polymer having the specified 35/65 substituent ratio. The chief difference is in the elastomeric properties of the cured polymer. The polymer used will be more plastic and less rubbery than anticipated. This should not effect the results that would be obtained from the IEEE 383 and Simulated Shipboard Passageway burning tests which is the primary reason for cable fabrication.

3.4 Cable Fabrication

3.4.1 Formulation Changes Due to Fabrication Requirements

Pilot plant produced and upgraded polymer was used to prepare 2-pound samples of the best cable covering formulation and wire covering formulation for evaluation by Boston Insulated Wire & Cable Company. The formulation and their vulcanizate properties are shown in Table XVIII and Table XIX.

TABLE XVIII

SAMPLES FOR BOSTON INSULATED WIRE & CABLE COMPANY

Formulation	Cable Covering	Wire Covering
Polymer	100	100
Hydral 705	90	--
Lubral Hydral 710	--	50
$Mg(OH)_2$	15	25
Silastic HA-2	10	10
Irganox 1010	0.5	0.5
Zinc Hydroxyquinolate	0.5	0.5
Luperco 500 - 40KE	2	2.75

TABLE XIX

PROPERTIES OF TABLE XVIII VULCANIZATES

Property	Cable Covering	Wire Covering
Tensile strength, psi	900	830
Elongation at break, %	235	290
Hardness, Shore A	47	35
LOI, ASTM D 2863	43	34
Flame spread index, ASTM E 162	4	6
Pico abrasion index, ASTM D 2228	13.5	19.5
Brittle point, ASTM D 746	10° to 15°F	10° to 15°F

The samples were evaluated at Boston Insulated Wire & Cable Company. They felt that the uncured stock is too soft and tacky to handle in their factory. Their suggestions were to reduce the tackiness, speed up the cure and increase hardness to Shore A values of 60 to 65. Tackiness was reduced somewhat and hardness brought up to suggested values by incorporation of 20 parts Hi-Sil 233 to the formulations. Cure was speeded up and hardness increased also by raising the peroxide level to 3 parts in the cable covering formulation and to 4 parts in the wire covering formulation. The Silastic HA-2 level was adjusted to 12.5 parts in the cable covering formulation only. Table XX shows the results of these changes.

TABLE XX

PROPERTIES OF REFORMULATED MIXES

Property	Cable Covering	Wire Covering
Tensile strength, psi	940	980
Elongation at break, %	170	190
Shore A	66	59

Table XX shows that the only undesirable change in physical properties is in the elongation at break.

The reformulated mixes were evaluated and found to be acceptable for use in production equipment. The cable covering formulation required some forced feeding of the extruder.

3.4.2 Large Scale Mixing

The two formulations, 130 pounds each, were mixed on a 60 inch two roll mill. Mill opening was varied as needed but was mostly in the range of 3/8 to 1/2 inch. Order of addition is not critical but the silicone should be added as soon as possible. Peroxide was added last and after incorporation the mix was given 4 cuts from each side then removed as slabs. The temperature of the mixes was 40 to 45° C. Total time for each was about 75 minutes.

There was a large amount of dusting and future work might best be done in an internal mixer such as a Banbury. Less than 1% of each mix was lost during the mixing. For both mixes

it was noted that solids were uniformly distributed but not broken down to their smallest particle sizes. Additional mixing will be needed. The cable fabricator was supplied with 126 pounds of each mix.

3.4.3 Properties of Large Scale Mixes

All tensile strength and elongation data are from ring specimen as per ASTM D 3196. The usual mix size prepared for developmental studies was 1/2 pound or less. It was noted that the 2 pound and 130 pound mixes had different responses to the peroxide level in them. The physical property data indicates that the peroxide level should be reduced in a large scale mix. Table XXI shows the results obtained from the final formulations at the 1/2, 2 and 130 pound scale. Also shown is the result of additional milling on the 130 pound mixes.

TABLE XXI

PHYSICAL PROPERTIES OF FINAL FORMULATIONS

Formulation	Cable Covering	Wire Covering
Polymer	100	100
Hydral 705	90	-
Lubral Hydral 710	-	50
$Mg(OH)_2$	15	25
Hi-Sil 233	20	20
Silastic HA-2	12.5	10
Irganox 1010	0.5	0.5
Zinc Hydroxyquinolate	0.5	0.5
Luperco 500-40KE	3	4

TABLE XXI (Continued)

Property	Lbs. of Mix	Cable Covering	Wire Covering
Tensile strength, psi		970	980
Elongation at break, %	1/2	215	205
Hardness, Shore A		66	58
Tensile strength, psi		940	1180
Elongation at break, %	2	170	125
Hardness, Shore A		66	66
Tensile strength, psi		1230	950
Elongation at break, %	130	85	95
Hardness, Shore A		73	68
Tensile strength, psi	130	1000	760
Elongation at break, %	(Extra	140	135
Hardness, Shore A	Milling)	68	62
Pico abrasion index, ASTM D 2228	2	28.2	19.0
Brittle point, ASTM D 746	2	15°-20°F	15°-20°F

The reformulation had essentially no effect on the Pico abrasion index of the wire covering compound. The index for the cable covering compound showed a marked improvement. As expected, the brittle point rose somewhat but the test, while giving a value for comparison purposes under the conditions of the test, does not necessarily measure the lowest temperature at which the material may be used.

All combustion properties were determined from final formulations as shown in Table XXI at the 2 pound scale of mixing.

TABLE XXII

COMBUSTION PROPERTIES OF FINAL FORMULATIONS

Property	Cable Covering	Wire Covering
LOI, ASTM D 2863	47	38
Flame spread index, I_s ASTM E 162	6	8
NBS Smoke Density, Dmc		
Smoldering	18	20
Flaming	49	75

Electrical properties were also determined from the final formulations at the 2 pound scale of mixing. Since the dielectric strength was very high, the dielectric constant and dissipation factor was measured at the usual 50 mils thickness and also at 25 mils to determine any effects due to sample thickness. The data indicates that a thinner wire covering would not have improved dielectric constant or dissipation factor.

TABLE XXIII

ELECTRICAL PROPERTIES OF FINAL FORMULATIONS

Property	Cable Covering	Wire Covering
Dielectric strength volts/mil ASTM D 149	> 730	> 870

Wire Covering (ASTM D 150)

Hz	Mils	Dielectric Constant	Dissipation Factor
10^2	26	5.50	0.0710
10^2	50	5.58	0.0710
10^4	26	4.88	0.0269
10^4	50	4.98	0.0233
10^6	26	4.36	0.0515
10^6	50	4.50	0.0485

3.5 Recommendations for Future Work

If the cable produced and tested under the present contract gives results that indicate the desirability for having a poly(phosphazene) wire and cable insulation, then the preparation of an improved polymer would be of primary importance. An improved polymer would be one of higher molecular weight, having a dilute solution viscosity of 1.5 to 1.6 dl/g. It would not require upgrading before use. It would have a phenoxy/4-ethylphenoxy substituent mole ratio of 35/65 $\pm$5 mole per cent. These improvements should allow the reduction or elimination of Hi-Sil 233 from the formulations. All the above should give a more rubbery composition with improved low temperature properties.

At the same time an improved polymer is being sought, some attention should be directed towards wet electrical properties. Time did not allow for formulation development and testing in this important area.

The behavior of the formulations with respect to large scale mixing equipment also needs investigation.

4.0 GLOSSARY

CUMAR P-10	Coumarone-indene resin (Neville Chem. Co.).
DBEP	Dibutoxyethyl phthalate (Armak).
DOP	Dioctyl phthalate (Ashland Chemicals).
Firebrake ZB	Zinc borate (U. S. Borax).
FR-515	Proprietary organic compound (Firetect, Inc.).
Hi-Sil EP	Precipitated hydrated silica (PPG Ind.).
HI-Sil 233	Precipitated hydrated silica (PPG Ind.).
Hyral 705	Very fine alumina trihydrate (Alcoa).
Irganox 1010	Multifunctional high molecular weight phenolic antioxidant (Ciba-Geigy Corp.).
Kenflex A	Aromatic hydrocarbon resin (Kenrich Petrochemicals, Inc.).
2% Lubral Hydral 710	Hydral 710 (coarser grade than 705) treated with 2% of a fatty acid derivative (Alcoa).
Luperco 101-XL	2,5-Dimethyl-2,5-bis(t-butylperoxy)hexane (Lucidol Div., Pennwalt).
Luperco 500-40KE	40% Dicumyl peroxide on clay (Lucidol Div., Pennwalt Corp.).
Silastic HA-2	A methylvinyl polysiloxane and dimethyl polysiloxane and a fine silica masterbatch (Dow Corning).
Solem 632-SP	Silane treated superfine hydrated alumina (Solem Industries).
USP 130-KXL	3,6,6,9,9-Pentamethyl-3-n-butyl-1,2,4,5-tetroxy-cyclononane on clay (Witco Chem.).
Vulcup 40KE	40% α,α'-bis(t-butylperoxy)diisopropyl-benzene on clay (Hercules).