TECHNICAL REPORT
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SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

by

Peter Dunn

Vincent S. Javier

CLOTHING & ORGANIC MATERIALS DIVISION

August 1965

U. S. Army Materiel Command
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts

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and

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FOREWORD

The Armed Services have a continuing need for high quality black and non-black rubber vulcanizates for military use. These low-cost general purpose rubbers should be capable of use over the temperature range from -50°C to +150°C and should have good long-term ozone, aging, and weathering resistance. The properties of the recently discovered ethylene-propylene diene (EPD) rubbers indicate that these materials could be suitable for many military requirements. Although EPD rubbers reinforced with carbon black have been extensively investigated, little work has been reported on high quality non-black EPD rubbers. The object of this project is to determine the properties of non-black EPD rubber vulcanizates and to evaluate their military potential.

This research was performed in the Rubber, Plastics, and Leather Engineering Branch, Clothing and Organic Materials Division, U. S. Army Natick Laboratories, Natick, Massachusetts, between May 1964 and March 1965. The research chemists assigned to the project were Mr. Peter Dunn and Mr. Vincent S. Javier. Mr. Dunn is employed at the Defence Standards Laboratories, Department of Supply, Melbourne, Australia. His research at the U. S. Army Natick Laboratories was sponsored by the Australian Government.

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ABSTRACT

High quality ethylene-propylene diene (EPD) rubber vulcanizates can be produced by using hydrated silica as the reinforcing filler. Modification of EPD rubber by chemical promotors such as p-quinone dioxime and the use of silica activators such as polyethylene glycol gives compounds with an acceptable rate of cure. Hot mastication, especially in the presence of halogenated compounds, gives vulcanizates with good physical properties. Processing aids such as stearic acid may be used, and oil-extended EPD rubber is a convenient plasticizer for silica-reinforced compounds.

To reduce costs, silica fillers can be extended with other such low-cost fillers as hard clay. EPD rubbers may also be blended with other elastomers. High quality silica-reinforced expanded EPD rubbers may be produced by conventional blowing agents and processing techniques. Silica-reinforced EPD rubbers crosslinked with organic peroxides give vulcanizates with good resistance to abrasion and compression set.

EPD rubber vulcanizates have excellent resistance to ozone and fungi and, in the presence of ultraviolet screening agents, show good weathering properties. It is expected that, in the future, ethylene-propylene diene rubbers will have many applications in military equipment.

SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

I. Introduction

Ethylene-propylene diene (EPD) rubber is a terpolymer of ethylene, propylene, and an unconjugated diene. It differs from ethylene-propylene copolymer rubber (EPR) in that the pendant unsaturation introduced by the diene monomer enables the rubber to be crosslinked by conventional sulphur vulcanizing techniques as well as by organic peroxides.

Although EPD rubber did not become commercially available until 1964, extensive compounding studies using carbon black fillers have already been undertaken and McCabe[1] has reviewed the five-year outlook for EPD rubber in the United States. EPD rubber is a high-performance, low-cost, general-purpose rubber which can be compounded to give vulcanizates with good resistance to heat, ozone, water, steam, acids, alkalis, alcohols, glycols, and phosphate esters. The vulcanizates have excellent electrical and dynamic properties as well as good resistance to aging and weathering. Because of these attractive properties, the U. S. Army Materiel Command is investigating the use of EPD rubber in applications such as coatings for synthetic fabrics[2], protective masks[3,4], and tank track pads[5]. It has also undertaken processing studies[6].

In the presence of strongly reinforcing fillers, such as carbon black[7], EPD rubbers yield vulcanizates of high modulus and tensile strength. In many applications where low cost, non-black color, or good electrical resistance is required, it is necessary to use mineral fillers. However, poorly reinforcing mineral fillers and amorphous EPD rubber yield vulcanizates which generally do not have the excellent stress-strain properties of compounds reinforced with carbon black.

This report describes the use of fine-particle-size silica as a non-black reinforcing filler for EPD rubber. It discusses the physical properties of these vulcanizates (which are excellent) and the potential use of silica-reinforced EPD rubbers in military equipment.

II. Materials

A. Commercially Available EPD Rubbers

At present, EPD rubbers are available from three major chemical companies in the United States. Details of the rubbers and their properties are given in Table I. In general, these data were obtained from the manufacturers' literature[8,9,10,11]. Each manufacturer uses a specific diene monomer, the type and amount of which has a marked effect on the processing and curing characteristics of the formulated compound.

Table I

PROPERTIES OF COMMERCIAL ETHYLENE-PROPYLENE DIENE RUBBERS PRODUCED IN THE USA

Trade Name	Nordel 1040	Nordel 1070	Nordel 1070E	Nordel 1145	Royalene 200	Royalene X300	Royalene X301	Royalene X400	Enjay 3509
Manufacturer	du Pont	du Pont	du Pont	du Pont	US Rubber	US Rubber	US Rubber	US Rubber	Enjay Chemical
Type	100% EPDR	100% EPDR	Oil-extended Oil: 50phr(1)	100% EPDR (Extrusion Grade)	100% EPDR	100% EPDR	100% EPDR	Oil-extended Oil: 100phr(1)	100% EPDR
Physical form	Slab(2)	Slab	Slab	Slab	Chips	Chips	Chips	Elastic crumb	Chips
Color and odor(3)	Amber	Amber	Dark amber	Amber to Light grey	Light amber	Light amber	Light amber	Light amber	Light amber
Standard package, lb	75	75	75	75	50	50	50	50	50
Ethylene, wt, %	53(4)	53(4)	53(4) phr	-	-	-	-	-	55
Diene monomer	1:4 Hexane-diene type	1:4 Hexane-diene type	1:4 Hexane-diene type	1:4 Hexane-diene type	Dicyclopen-tadiene type	Dicyclopen-tadiene type	Dicyclopen-tadiene type	Dicyclopen-tadiene type	Methylene nor-bornene type
Unsaturation, wt, %	2-3	2-3	2-3	2-3	2-3	2-3	2-3	2-3 phr	2.6
Iodine no.(g/100 g)	-	-	-	-	10	12	12	-	-
Ash, wt, %	-	-	-	-	-	-	-	-	0.3
Volatiles, wt, % (24 hr/100°C)	0.7	0.7	0.7	0.7	-	-	0.6	0.6	0.3
Stabilizer, wt, %	-	-	-	-	0.5	1.0	1.0	1.0 phr	0.25(5)
Specific gravity	0.85	0.85	0.88	0.85	0.865	0.865	0.865	0.897	0.86
Cost, cents per lb	30	30	-	30	30	30	30	20	30
Refractive index	1.481-1.484	1.481-1.484	-	1.481-1.484	-	-	-	-	-
Coefficient of linear expansion, $(^{\circ}C)^{-1}$	2.3×10^{-4}	2.3×10^{-4}	-	2.3×10^{-4}	-	-	-	-	1.6×10^{-4}
Intrinsic viscosity	2.5-2.7(6)	-	-	-	-	-	-	-	2.7-3.3(7)
Mooney viscosity ML(1 + 4)									
212°F	48	80	36	63	140	130	60	60	87
250°F	40	70	30	45	-	-	52	70	62

Notes:
(1) Naphthenic process oil
(2) Exhibits some cold flow
(3) No significant odor present
(4) Ref. 11
(5) Parabar 441, Enjay Chemical Company. A non-staining butylated hydroxy toluene
(6) At 25°C: 0.1% solution in tetrachloroethylene (w/v)
(7) At 135°C: 1.0% solution in decalin (w/v)

B. Silica Reinforcing Fillers

Among the mineral fillers, such as hard and soft clays, whitings, talcs, silicates, and aluminates, that have been evaluated as reinforcing fillers for EPD rubbers[8,9,10,12,13], only fine-particle-size silicas have a reinforcing effect equal to that of carbon black. The review by Bachmann and coworkers[14] describes the properties and reinforcing action of the commercially available silicas and silicates.

In the United States, one low-cost readily available precipitated hydrated silica of very fine ultimate particle size is Hi-Sil 233[15]. A compacted form is available as Hi-Sil 215[16]. Bartrug and Meltz[17] have shown that Hi-Sil 233 can be used to produce high quality, non-black EP rubber vulcanizates. At the Natick Laboratories, we used Hi-Sil 233 as the reinforcing filler for EPD rubber vulcanizates.

C. Miscellaneous Compounding Materials

The compounding materials used were commercial products obtained from recognized suppliers[18]. Details are given in Appendixes I and II. Other compounding materials comparable in chemical composition and activity should prove to be equally satisfactory.

III. Experimental

All of the rubber compounds were processed on conventional rubber compounding equipment. Whenever possible, rubber masterbatches were mixed on a 20- by 10-inch variable-speed two-roll mill, while hot mixing and final compounding were carried out on 12- by 6-inch two-roll mills. Test sheets were vulcanized in 4-cavity chrome-plated molds in a steam-heated press.

Standard testing equipment was used. The test methods are listed in Appendix III.

Outdoor exposure tests were carried out at Natick where samples were exposed facing south at an angle of 45°. Water leaching, accelerated weatherometer exposures, and soil burials were undertaken by the United States Testing Company at Hoboken, New Jersey. These vulcanizates were returned to the Natick Laboratories for evaluation.

IV. Results and Discussion

A. Curing Systems for Silica-Reinforced EPD Rubbers

1. Sulphur systems

In EPD rubbers, the level of unsaturation selected allows vulcanization with a variety of curing systems commonly used with other general purpose elastomers. As the level of unsaturation of EPD rubbers is similar to that found in butyl rubber, the sulphur and accelerator combinations suitable for curing butyl are also generally effective with the EPD rubbers. Combinations of sulphur with such accelerators as thiuram disulphide and dithiocarbamates will vulcanize EPD rubber when used in conjunction with thiazole-type compounds. Organic peroxides[24] and phenolic resins[21,25] are also effective crosslinking agents. Natta and coworkers[19], Auda and coworkers[20,21], Roche[22], and others[7,8,9,10,23,29] have discussed the selection of a suitable sulphur-type curing system for carbon black and mineral-filled EPD rubbers.

Curing systems based on zinc oxide, sulphur, tetramethylene thiuram tetrasulphide (TMTD), dipentamethylenethiuram tetrasulphide (DPMTT), and mercaptobenzothiazole (MBT) give satisfactory bloom-free vulcanizates. Those based on DPMTT are known to give vulcanizates with good heat resistance also[26,27]. On the other hand, vulcanizates with non-sulphur crosslinkages obtained from resin, quinoid, and peroxide curing systems display maximum heat- and compression-set resistance.

For the development of tensile properties, the optimum sulphur level of the curing system was found to be 2 phr. This generally gave the maximum degree of crosslinking, as assessed by the highest stress at 300 percent elongation and the lowest ultimate elongation. Higher levels of sulphur caused excessive bloom while lower levels tended to decrease the state of cure.

The optimum time and temperature for curing commercial EPD rubbers with zinc oxide (5 phr), sulphur (2 phr), TMTD (0.75 phr), DPMTT (0.75 phr), and MBT (1.5 phr) was found to be 20 minutes at 160°C. This gave bloom-free vulcanizates with good physical properties. Longer cure times gave vulcanizates with improved compression set, modulus, and abrasion resistance, and with no tendency to reversion. Curing systems based on zinc dimethyl dithiocarbamate (ZDC) may be used with EPD rubber[8,9,10,22], but many of these vulcanizates show a marked tendency to bloom.

The properties of vulcanizates based on Nordel 1040 and Enjay 3509 are given in Table II. Royalene EPD rubbers can be compounded to give vulcanizates with equivalent physical properties using other curing systems[10]. The presence of either dioctyl sebacate or a naphthenic oil plasticizer does not markedly affect the activity of the curing system (Section IV, B3).

2. Effect of "ultra" accelerators

In order to develop EPD compounds with a fast rate of cure, "ultra" accelerators such as metal- containing dithiocarbamates may be used. Copper dimethyl dithiocarbamate or tellurium diethyl dithiocarbamate are

TABLE II

EFFECT OF EPD RUBBER TYPE ON VULCANIZATE PROPERTIES

Compound	1	2	3	4
Formulation*:				
Nordel 1040 EPD rubber	100	-	80	-
Enjay 3509 EPD rubber	-	100	-	80
Royalene X400 EPD rubber	-	-	40**	40**
Dioctyl sebacate	20	20	-	-
Tensile strength, psi	3100	2700	3300	3275
Ultimate elongation, %	600	530	540	570
Stress at 300% elongation, psi	1000	1150	1200	1200
Hardness, Shore "A"	64	61	62	63
Abrasive index, NBS	210	283	275	286
Compression set, %, after				
24 hr at room temperature	14.3	11.7	8.6	11.9
24 hr at 100°C	71.0	67.7	71.0	73.3
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	300	250	200	70

*Formulation: EPD rubber and dioctyl sebacate as listed; Hi-Sil 233, 50; polyethylene glycol 4000, 1; stearic acid, 1; p-quinone dioxime, 1; chlorosulphonated polyethylene 7.5; HAF black, 3. Compounds 1 and 3 hot-milled 10 min at 160°C; compounds 2 and 4 hot-milled 5 min at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds cured 20 min at 160°C.

**Equivalent to 20 phr of EPD rubber and 20 phr of naphthenic oil.

effective accelerators for EPD rubbers. While their color precludes their use in light colored stocks, they can be used in olive-drab EPD rubbers. Copper 8-hydroxy quinolinolate, a known fungicide for many synthetic rubbers, is also an effective accelerator for sulphur-cured EPD rubbers (Section IV, E). Where fast-curing light-colored stocks are required, cadmium diethyl dithiocarbamate may be used. A cure time of 10 minutes at 160°C is sufficient in many cases to give vulcanizates with acceptable physical properties. Zinc dimethyl or diethyl dithiocarbamate also gives fast-curing systems with variable bloom characteristics that need to be investigated for each specific compound.

3. Peroxide systems

In sulphur-cured EPD rubbers, the number of double bonds available limits the degree of crosslinking. Peroxide curing agents, however, can react with any of the tertiary hydrogens on the propylene groups to give vulcanizates with a greater number of crosslinks. Peroxide-cured EPD rubbers give light-colored vulcanizates with excellent resistance to heat aging and compression set. McGarvey and Veroeven[5] and Sieron[27] have shown that peroxide-cured compounds may be used at temperatures of up to 200°C.

In ethylene-propylene copolymer (EP) rubbers, unsaturated coagents can be used with organic peroxides to improve crosslinking efficiency[28]. Howarth, Cornell, and Olsen[24] have shown that similar improvements can apply to peroxides used to cure EPD rubbers. Although sulphur is an effective coagent for carbon black reinforced EP rubber, it is not effective in silica-reinforced EP or EPD rubbers. Similarly, DPMTT (1 phr), alone or in combination with triallyl cyanurate (1 phr), does not markedly improve the crosslinking efficiency of dicumyl peroxide.

Unsaturated crosslinking coagents, such as ethylene glycol dimethacrylate or trimethylolpropane trimethacrylate (TMPTM), are effective coagents for dicumyl peroxide. Details of rubbers crosslinked with sulphur and also with peroxides are given in Table III.

Although hot milling (Section IV, B) is very effective in improving the properties of sulphur-cured EPD rubbers (Table III, compounds 5, 7), it is less effective in rubbers cured with peroxides (compounds 6, 8). Hot milling Nordel 1040 rubber in the absence of p-quinone dioxime, followed by crosslinking with dicumyl peroxide and TMPTM, gives vulcanizates with inferior physical properties. Similar cold-milled rubbers have a very slow rate of cure. Activators as well as coagents for the peroxides are required for use with silica-reinforced EPD rubbers. Tetraethylthiuram disulphide (TETD) is effective in Enjay 3509, and p-quinone dioxime in Nordel 1040.

TABLE III

PROPERTIES OF SULPHUR- AND PEROXIDE-CURED EPD RUBBERS

Compound*	5	6	7	8	9**	10**
EPD rubber	Enjay 3509	Enjay 3509	Enjay 3509	Enjay 3509	Nordel 1040	Nordel 1040
Time of hot milling	Nil	Nil	10'/121°C	10'/121°C	Nil	10'/160°C
Curing system	Sulphur	Peroxide	Sulphur	Peroxide	Peroxide	Peroxide
p-Quinone dioxime, phr	-	-	-	-	1.0	1.0
Tetraethylthiuram disulphide, TETD, phr	1.0	1.0	1.0	1.0	-	-
Mooney properties at 138°C:						
time to scorch, min (5 pts rise)	7.0	7.3	9.0	8.5	8.5	4.0
Minimum viscosity, points	116	115	88	80	82	66
Cure index, Δ 30, min	1.4	4.6	2.5	3.2	5.4	1.4
Mooney viscosity, ML(1+4), 121°C	118	119	97	93	88	70
Tensile strength, psi	2600	2550	3400	2300	2200	1900
Ultimate elongation, %	650	570	570	520	580	580
Stress at 300% elongation, psi	600	850	1200	1100	900	800
Hardness, Shore "A"	72	70	68	64	68	60
Abrasive index, NBS	123	204	179	348	173	1000+
Compression set, %, after						
24 hr at room temperature	13.6	11.7	11.8	8.9	9.6	11.8
24 hr at 100°C	76.6	22.8	68.3	18.2	27.3	26.7
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	100	200	60	125	125	40

*Formulation: EPD rubber as shown, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; Hi-Sil 233, 50; polyethylene glycol, 1; stearic acid, 1. p-Quinone dioxime and TETD as shown. Compounds hot milled as shown.

Curing systems: sulphur system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5

peroxide system: dicumyl peroxide (40%), 9.0; trimethylolpropane trimethacrylate, 3.0.

All compounds cured 20 minutes at 160°C.

**Compare to compound 3, Table II.

As shown in Table III, peroxide-cured EPD rubbers have a greater resistance to compression set at elevated temperatures than similar rubbers cured with sulphur. Hot- or cold-milled peroxide-cured compounds based on Enjay 3509 are suitable for use in white or light-colored stocks (compounds 6,8), while similar compounds based on Nordel 1040 are suitable for black or dark-colored stocks (compounds 9, 10), especially where maximum abrasion resistance is required.

B. Silica Reinforcement of EPD Rubbers

1. Hot milling with fine-particle-size silica

As non-crystallizing elastomers, unfilled vulcanizates of EPD rubber have very low tensile strength. Reinforcing silica fillers impart high strength to the rubbers but adequate dispersion of the silica and the rubber is necessary to obtain the maximum reinforcing effect. As with butyl rubber[14], the state of cure of silica-filled rubbers can be improved by hot milling the filler and oil with the base rubber at temperatures of up to 200°C and in the presence of a chemical promotor. The proper milling temperature is important as some degradation can occur with such fillers as hard clay when mixed at temperatures in excess of 130°C .

Silica fillers can readily be incorporated into EPD rubber by hot milling either on a heated open roll mill or in an internal mixer. As shown in Figures 1 and 2, hot milling of Nordel 1040 for 10 minutes at 160°C gives vulcanizates with good physical properties, although milling temperatures as high as 200°C may be used[22]. Hot milling results in a modification of the silica structure and improved wetting between the filler and the polymer. While, in general, tensile strength, modulus, and abrasive index are increased by hot milling, tear strength is reduced. With Enjay 3509, hot milling for 5 minutes at 160°C (or 10 minutes at 120°C) is sufficient to give vulcanizates with good physical properties (Table II, compounds 2 and 4).

Maximum benefit from hot milling was obtained when the reinforcing filler (Hi-Sil 233), lubricating agent (stearic acid), pigment (carbon black), silica activator (polyethylene glycol), and other additives (p-quinone dioxime and chlorosulphonated polyethylene) were all included in the hot milling cycle. The zinc oxide, sulphur, and accelerators were added later at normal mixing temperatures.

2. Effect of heat promotors

For maximum physical properties in silica-reinforced EPD rubbers, hot milling in the presence of a heat promotor is necessary Promotors such as p-quinone dioxime, N-Me-N4 dinitrosoaniline (33% active) (MDNA), and dibenzo-p-quinone dioxime are all very effective. These

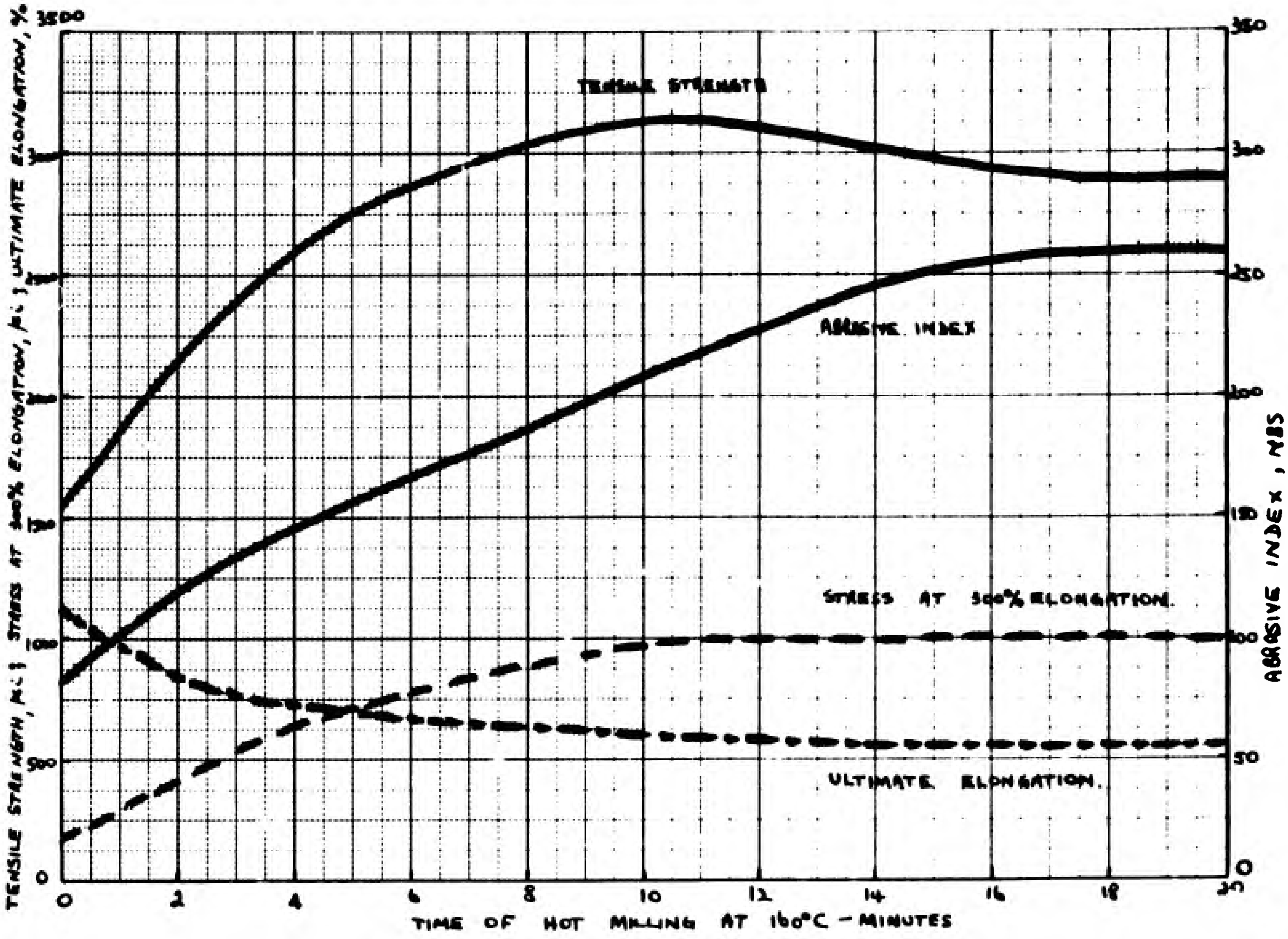

Figure 1. Effect of time of hot milling on the physical properties of silica-reinforced EPD rubber

Formulation: Nordel 1040, 100; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; polyethylene glycol, 1; p-quinone dioxime, 1; dioctyl sebacate, 20. Compounds hot-milled at 160°C for the times listed.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPTT, 0.75; MBT, 1.5. Compounds were press cured for 20 minutes at 160°C.

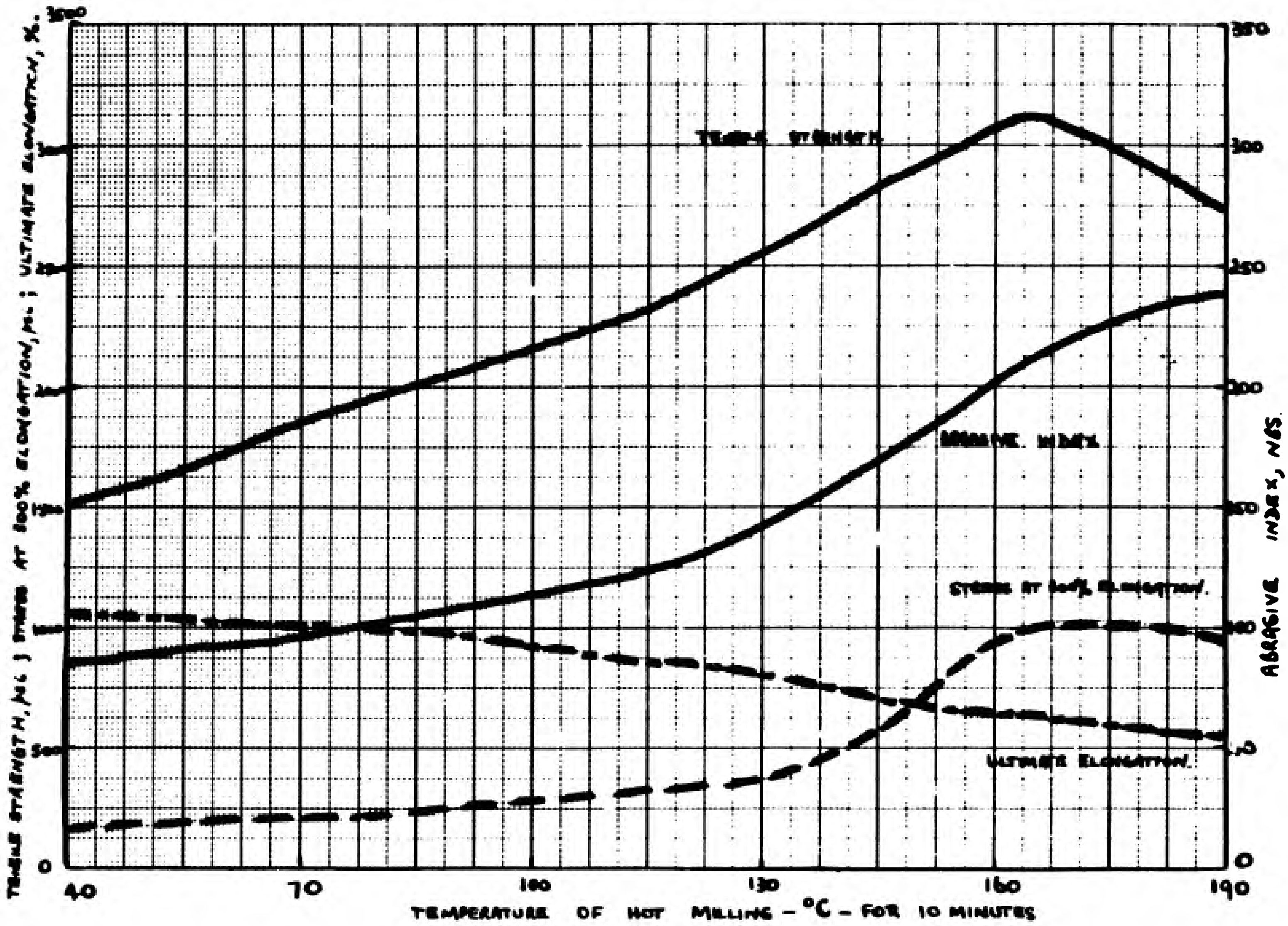

Figure 2. Effect of temperature of milling on the physical properties of silica-reinforced EPD rubber

Formulation: Nordel 1040, 100; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; polyethylene glycol, 1; p-quinone dioxime, 1; dioctyl sebacate, 20. Compounds hot-milled at the temperature listed for 10 minutes.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds were press cured for 20 minutes at 160°C.

promotors give brown colored stocks, hence their use should be restricted to black or dark colored vulcanizates. DPMTT, TETD, diphenyl guanidine (DPG), 4,4'-dithio-dimorpholine (DTDM), and hexamethoxymethyl melamine (HMMM) are also effective and are non-discoloring heat promotors.

As shown in Figure 3, p-quinone dioxime used at the 1 phr level is an efficient chemical promotor for hot-milled EPD rubbers plasticized with dioctyl sebacate. Higher levels of p-quinone dioxime seriously retard the curing system and give vulcanizates with inferior properties. However, the use of variable amounts of this heat promotor provides a convenient and easy way of adjusting the rubber viscosity and modulus of silica-reinforced compounds to almost any desired level. p-Quinone dioxime is also an efficient chemical promotor for silica-reinforced EPD rubbers plasticized with naphthenic oils.

The efficiency of several chemical promotors in hot- and cold-milled EPD rubbers is shown in Table IV. In the cold-milled Nordel 1040 EPD rubber, p-quinone dioxime seriously retards the cure. DPMTT, MDNA, DPG, and HMMM do not show any marked effect in cold-milled compounds. TETD and DTDM, however, improve the rate of cure of cold-milled compounds and give light colored, bloom-free vulcanizates when used at the optimum concentration of 1 phr.

With hot-milled compounds, all the promotors listed in Table IV are effective in improving the rate of cure and give vulcanizates with good physical properties. Hot-milled compounds show lower Mooney viscosities and better flow properties than cold-milled compounds. For black or dark colored rubbers, hot milling with p-quinone dioxime (1 phr) is suitable, while for white or light colored rubbers, hot milling in the presence of TETD (1 phr) or DTDM (1 phr) is recommended. As shown in Figures 1 and 2, the optimum time of hot milling was 10 minutes at 160°C.

3. Plasticizers for EPD rubbers

Generally, petroleum oil plasticizers, which are highly compatible with EPD rubbers, can be added in large quantities with only a moderate reduction in the physical properties of the rubber. The processing oils should be saturated, if possible, otherwise the double bonds present will scavenge the sulphur used in the vulcanization. White[30] and others[31] discuss the basic rules for selecting suitable plasticizers and extenders for EPD rubber and show that the physical properties of the vulcanizates will vary with the type and viscosity of the compounding oils.

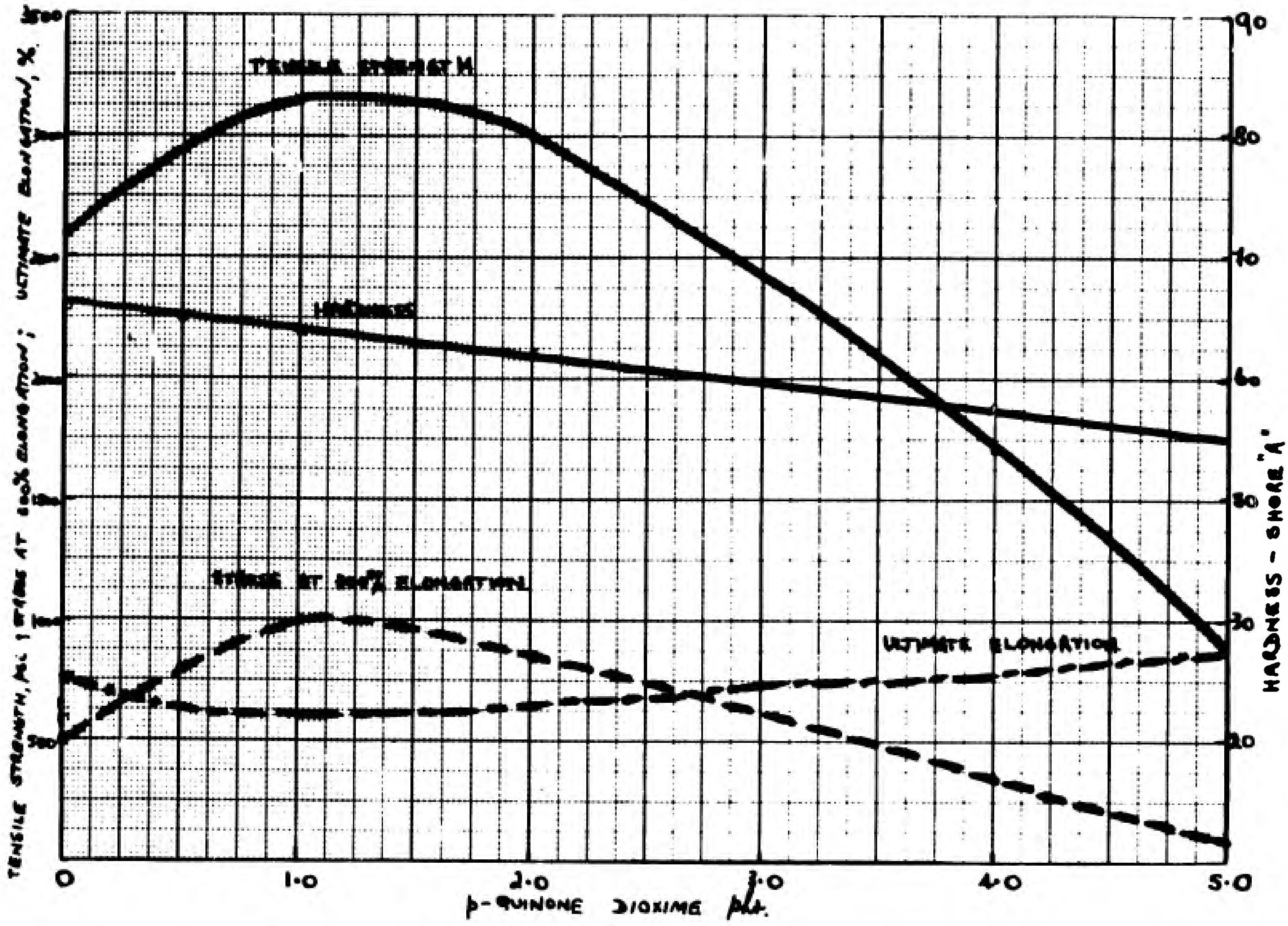

Figure 3. Effect of p-quinone dioxime concentrations on the physical properties of silica-reinforced EPD rubber

Formulation: Nordel 1040, 100; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; polyethylene glycol, 1; dioctyl sebacate, 20; p-quinone dioxime, as listed. Compounds hot-milled for 10 minutes at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds press cured 20 minutes at 160°C.

TABLE IV

EFFECT OF ORGANIC PROMOTORS ON HOT- AND COLD-MILLED EPD RUBBERS

	Compound*	11	3	12	13	14	15
	Promotor**	Nil	p-Quinone dioxime	DPMTT	MDNA	TETD	HMMM
	Concentration, phr	-	1.0	1.0	3.0	1.0	2.0
Compounds cold milled	Mooney properties at 138°C:						
	Time to scorch, min, (5 pts rise)	7.8	13.1	7.8	9.4	7.4	9.5
	Minimum viscosity, points	80	76	72	74	72	75
	Cure index, Δ30, min	2.2	34.5	1.7	3.2	1.4	2.0
	Tensile strength, psi	2900	1000	3250	2500	3050	2500
	Ultimate elongation, %	870	1000+	750	950	680	800
	Stress at 300% elongation, psi	325	100	270	350	600	400
	Hardness, Shore "A"	68	68	68	65	67	68
Compounds hot milled 10 min at 160°C	Mooney properties at 138°C:						
	Time to scorch, min, (5 pts rise)	11.3	11.3	9.5	10.7	9.8	12.9
	Minimum viscosity, points	50	62	60	54	52	54
	Cure index, Δ30, min	4.1	4.2	3.1	3.8	3.0	4.6
	Tensile strength, psi	3100	3400	3280	3380	3200	2800
	Ultimate elongation, %	700	540	640	600	630	600
	Stress at 300% elongation, psi	500	1200	750	1000	830	850
	Hardness, Shore "A"	60	60	60	56	59	64

*Formulation: Nordel 1040, 80, Royalene X400, 40; Hi-Sil 233, 50; polyethylene glycol, 1; stearic acid, 1; chlorosulphonated polyethylene, 7.5. Promotor and hot and cold milling as listed.
Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. All compounds press cured 20 minutes at 160°C.

**DPMTT, dipentamethylenethiuram tetrasulphide
MDNA, N-Me-N4 dinitrosoaniline (33% active)
TETD, tetraethylthiuram disulphide
HMMM, hexamethoxymethyl melamine

Recently, oil-extended EPD rubbers have been introduced (Table I) and Whitehouse, Barnhart, and Michell[32], also Luh[33], have discussed the properties of these new rubbers. Royalene X400, an EPD rubber extended with 100 phr of naphthenic oil, is a convenient plasticizer for silica-reinforced EPD vulcanizates, and dioctyl sebacate has been used as a general purpose plasticizer as well. Oil-extended EPD rubber may also be used to improve the ozone resistance of silica-reinforced styrene-butadiene rubbers (Section IV, C,4).

Silica-reinforced EPD rubbers (for example, compound 3) with naphthenic or paraffinic oils, di-2-ethyl sebacate, adipate, azelate, phthalate, or polyether plasticizers, give vulcanizates with similar properties. The tri-2-ethylhexyl phosphate plasticizer slightly retards the curing system but is preferred, along with di-2-ethylhexyl sebacate, when flexibility at low temperatures is important (Section IV, D). The tricresyl phosphate plasticizer is not compatible with EPD rubber and methylated tall oil ester plasticizers seriously retard the curing system. Since silica-reinforced EPD rubbers need to be hot milled to develop maximum physical properties, low-volatility plasticizers should be used. General purpose EPD rubber compounds, hot-milled for 10 minutes at 160°C, show a loss in weight of about 2.0 percent.

4. Effect of silica activators and stearic acid

In order to develop an adequate rate of cure in silica-reinforced rubbers, it is necessary to use a glycol or similar type of polyhydric compound[8,9,14]. When water (or a volatile glycol) is driven off at high processing temperatures, undercures are likely to occur[34]. Recently, however, Bartrug[35] has stated that special activators, such as diethylene glycol, are to be avoided in silica-reinforced EPD rubbers if maximum reinforcement is to be obtained, as they interfere with the filler-polymer interaction.

Examination of a series of silica activators, such as diethylene glycol, polyethylene glycol, pentaerythritol 200, triethanolamine, and bis (hydroxymethyl) 1,4-cyclohexane, has shown that these compounds are all effective in improving the properties of silica-reinforced EPD rubbers. The results given for compound 3 in Table IV are typical. Generally, silica activators are added at the level of 6 percent of the silica loading[8,9]. However, optimum physical properties are obtained at an activator level of about 2 percent of the silica loading (1 phr of activator per 50 phr of Hi-Sil 233). Higher levels of silica activators result in a reduction of physical properties. Polyethylene glycol and bis (hydroxymethyl) 1,4-cyclohexane are effective in silica-reinforced EPD rubbers plasticized with either naphthenic oils or ester-type plasticizers. Activators based on polyalkanolpolyamines generally retard curing systems based on zinc oxide, sulphur, TMTD, DPMTT, and MBT.

The presence of stearic acid is not essential for good vulcanization but small amounts (1 phr) improve processability and dispersion of the fillers, especially at high loadings. In the absence of stearic acid, there is no marked improvement in the physical properties of the EPD rubber vulcanizates.

5. Use of special additives

The rate of cure of mineral-filled EPD rubbers can be improved by the addition of polar rubbers such as chlorosulphonated polyethylene[22,36], or of other chlorine-containing compounds. Improvements are obtained in the scorch rate, compression set, permanent set, and stress at 300 percent elongation. The addition of chlorosulphonated polyethylene also gives vulcanizates with the maximum heat resistance, especially when used in conjunction with antimony trioxide[27] and high levels of zinc oxide[26]. In addition to covulcanizing with the EPD rubber, chlorosulphonated polyethylene is believed to give a large increase in the modulus due to reaction between the chlorine and chlorosulphonyl groups and the active groups on the surface of the silica filler.

The addition of chlorosulphonated polyethylene (7.5 phr) or octachlorocyclopentene (1.5 phr) to hot-milled silica-reinforced EPD rubber plasticized with either dioctyl sebacate or a naphthenic oil gives the maximum improvement in general physical properties. Chlorine-containing compounds, such as polychloroprene (7.5 phr), polyepichlorohydrin (7.5 phr), nitrile-polyvinylchloride resin blend (7.5 phr), p-toluene sulphonyl chloride (2.0 phr), hexachloroethane (2.0 phr), and dichlorodiphenyl-trichloroethane (2.0 phr), are not effective in improving the cure rate of silica-reinforced EPD rubbers. Perchloropentacyclodecane (7.5 phr), a known flame-proofing agent for ethylene-propylene copolymer rubber (EPR)[37], also has no effect on the cure rate.

Both chlorinated paraffin wax (7.5 phr) and tetrachloro-p-benzoquinone (2.0 phr) improve the rate of cure of silica-reinforced EPD rubbers but are not as effective as chlorosulphonated polyethylene or octachlorocyclopentene. These chlorine-containing additives are effective with both Nordel 1040 and Enjay 3509 EPD rubbers and give the maximum improvement in physical properties when used with hot-milled silica-reinforced compounds. The additives have no effect on the processing characteristics of EPD compounds, but both chlorosulphonated polyethylene and octachlorocyclopentene give improvements in the compression-set resistance of EPD rubbers at room temperature and at 100°C.

In the absence of a chemical promotor such as p-quinone dioxime, chlorosulphonated polyethylene (7.5 phr) or octachlorocyclopentene (1.5 phr) improves the physical properties of EPD rubbers and can be used for the production of white and light colored stocks. The combined use of these two chlorine-containing compounds in hot- or cold-milled EPD rubbers, as compared to their use individually, does not result in any improvement in physical properties. When rubbers with non-corrosive and non-staining properties towards metals are required, chlorine-containing additives should not be used.

Chemical analysis (C,H,N,Cl) of EPD rubbers, hot milled in the presence of p-quinone dioxime (1 phr) and octachlorocyclopentene (1 phr), alone and together, followed by purification by precipitation with methanol from a toluene solution (5% w/v), indicated that there was no chemical bonding between the additives and the polymer as a result of the hot milling process.

Recently Wolfe and Albin[38] have described the use of polyisocyanates as curing adjuvants for EPD rubbers. Compounds such as polymethylpolyphenylisocyanate (PMPPI) are effective in improving the cure rate, ultimate elongation, modulus, and compression-set characteristics of silica-reinforced EPD rubbers. The improvements in vulcanizate properties are believed to be due to a more effective reinforcement of the polymer by the filler. PMPPI added with the curing agents at the 3 phr level is very effective in improving the properties of hot-milled, silica-reinforced compounds activated with p-quinone dioxime (Table V, compound 16). Cure times of 10 minutes at 160°C give vulcanizates with good general physical properties.

In the absence of p-quinone dioxime, PMPPI is also effective for use with light colored stocks. The addition of PMPPI (3 phr) during the hot milling cycle does not result in any marked improvement in physical properties of the vulcanizates. For best results, the PMPPI is added, in the cold, along with the curing agents. As with most silica-reinforced rubbers, hot milling the rubber and the silica (compound 17) gives vulcanizates with superior physical properties to the cold-milled compound (compound 18). Details of vulcanizates containing PMPPI are given in Table V.

C. Physical Properties of EPD Rubbers

1. Silica-reinforced vulcanizates

Fine-particle-size silica fillers can be incorporated by up to 80 phr into EPD rubbers to give vulcanizates with good physical properties. At silica loadings above 60 phr, some retardation of the rate of cure can occur and longer cure times are necessary to obtain optimum properties in the vulcanizates.

Compounds plasticized with naphthenic oils, incorporated in the form of Royalene X400, have properties that are superior to those of vulcanizates containing the same amount of plasticizer incorporated in the form of a naphthenic light process oil. Figure 4 illustrates the physical properties obtained from a wide range of compounds containing hydrated silica filler and naphthenic

TABLE V

USE OF POLYMETHYLPOLYPHENYLISOCYANATE (PMPPI) IN EPD RUBBERS

Compound*	16	17	18
p-Quinone dioxime, phr	1	-	-
Time of hot milling at 160°C, min.	10	10	Nil
Mooney properties at 138°C·			
Time to scorch, min (5 pts rise)	12.9	10.2	12.6
Minimum viscosity, points	78	65	74
Cure index, Δ30, min	3.7	3.5	3.2
Mooney viscosity, ML(1+4), 121°C	80	98	70
Cured 10 min at 160°C			
Tensile strength, psi	2950	2600	2900
Ultimate elongation, %	540	650	840
Stress at 300% elongation, psi	1175	700	500
Hardness, Shore "A"	64	64	68
Cured 20 min at 160°C			
Tensile strength, psi	2900	3000	3200
Ultimate elongation, %	420	560	740
Stress at 300% elongation, psi	1700	1050	700
Hardness, Shore "A"	66	64	67
Abrasive index, NBS	269	247	167
Compression set, %, after			
24 hr at room temperature	8.6	11.3	10.7
24 hr at 100°C	63.5	69.8	74.6
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	200	100	50

*Formulations: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; polyethylene glycol, 1; stearic acid, 1; Hi-Sil 233, 50. p-Quinone dioxime and hot milling as shown. PMPPI, 3, and curing agents added on a cold mill.

Curing System: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DMPTT, 0.75; MBT, 1.5

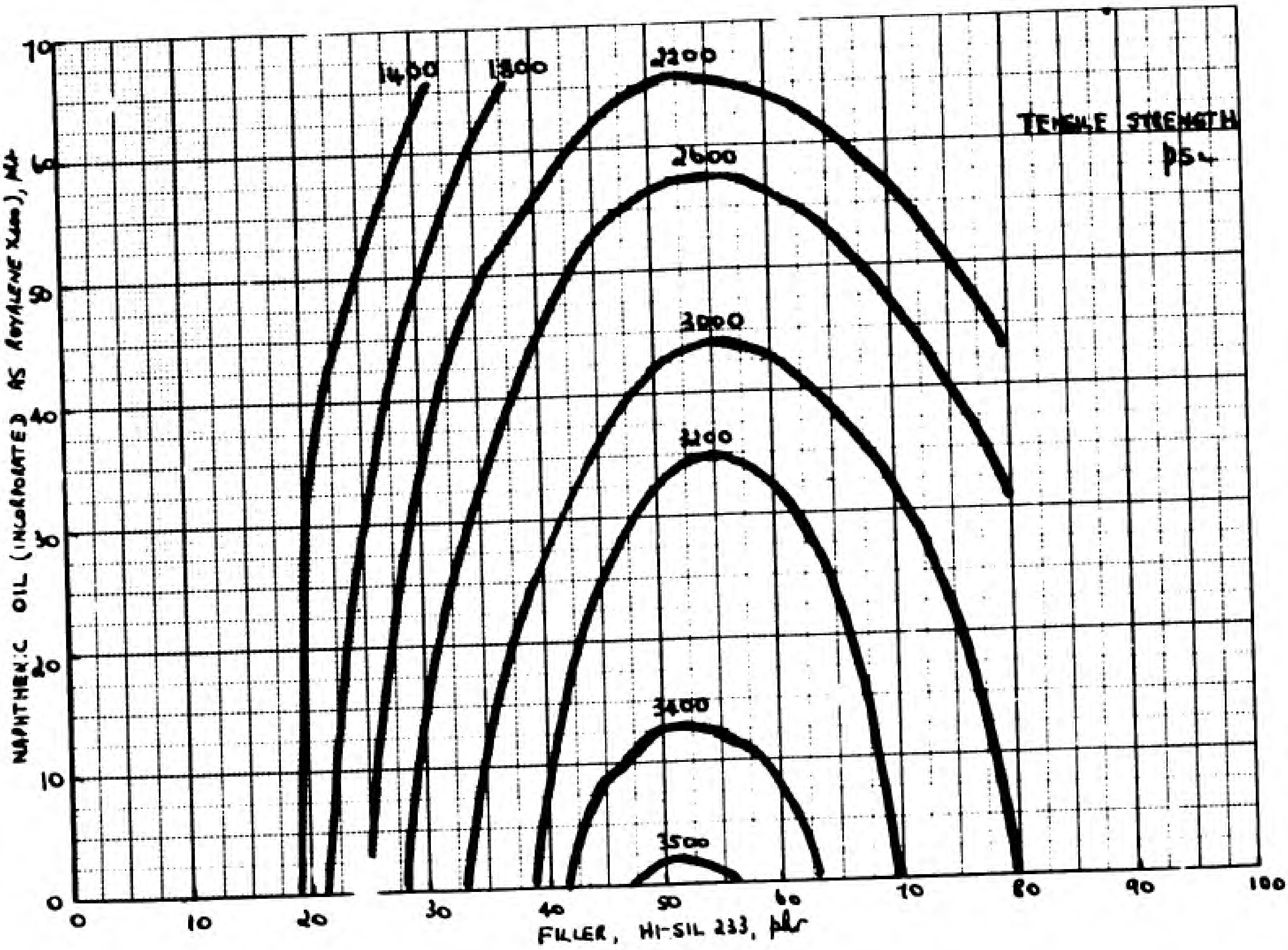

Figure 4a. Tensile strength, psi, of EPD rubbers at varying concentrations of silica and naphthenic oil

Formulation: Nordel 1040, 100-W; Royalene X400, 2W (W is naphthenic oil loading as shown; chlorosulphonated polyethylene, 7.5; Hi-Sil 233 as shown; polyethylene glycol, 2% of the Hi-Sil 233 loading; HAF black, 3; stearic acid, 1; p-quinone dioxime, 1. Compounds hot milled for 10 minutes at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Compounds press cured for 20 minutes at 160°C.

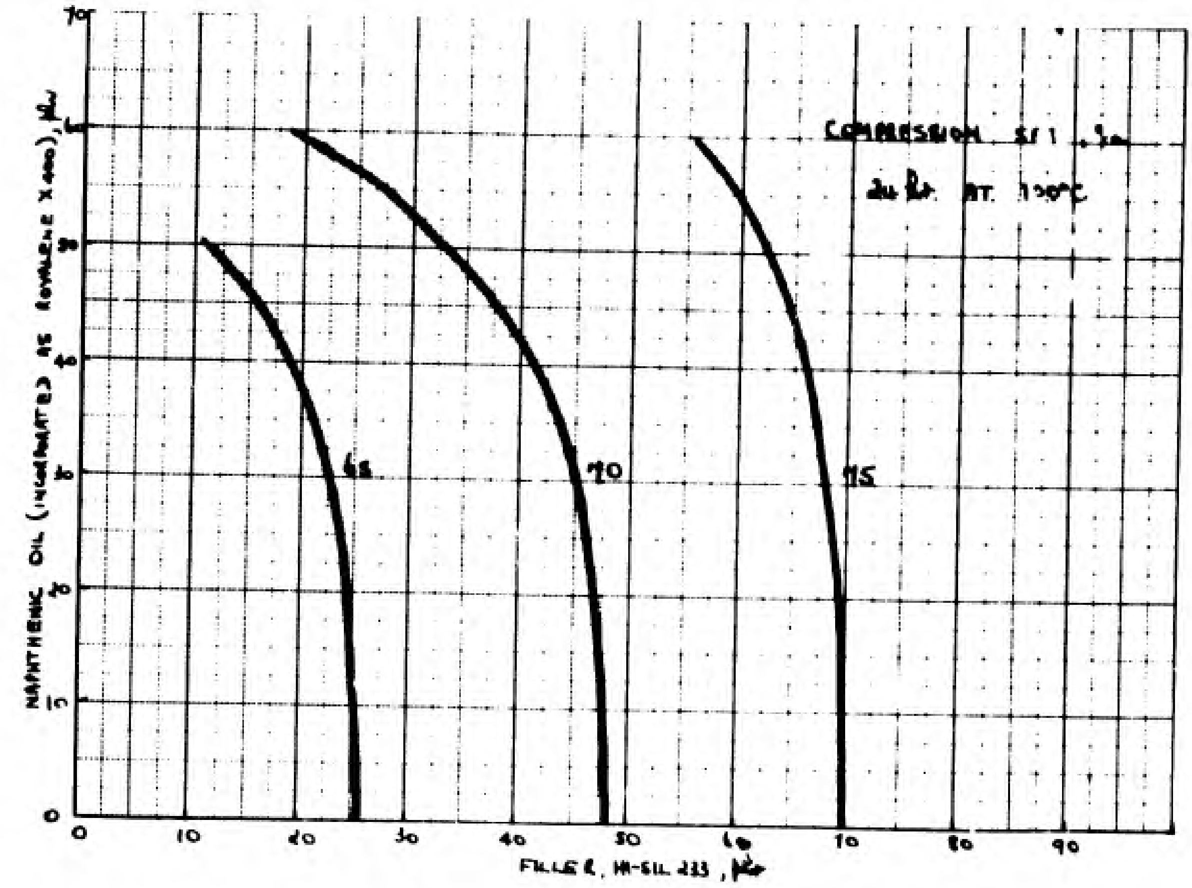

Figure 4b. Compression set, 24 hr at 100°C, %, of EPD rubbers at varying concentrations of silica and naphthenic oil

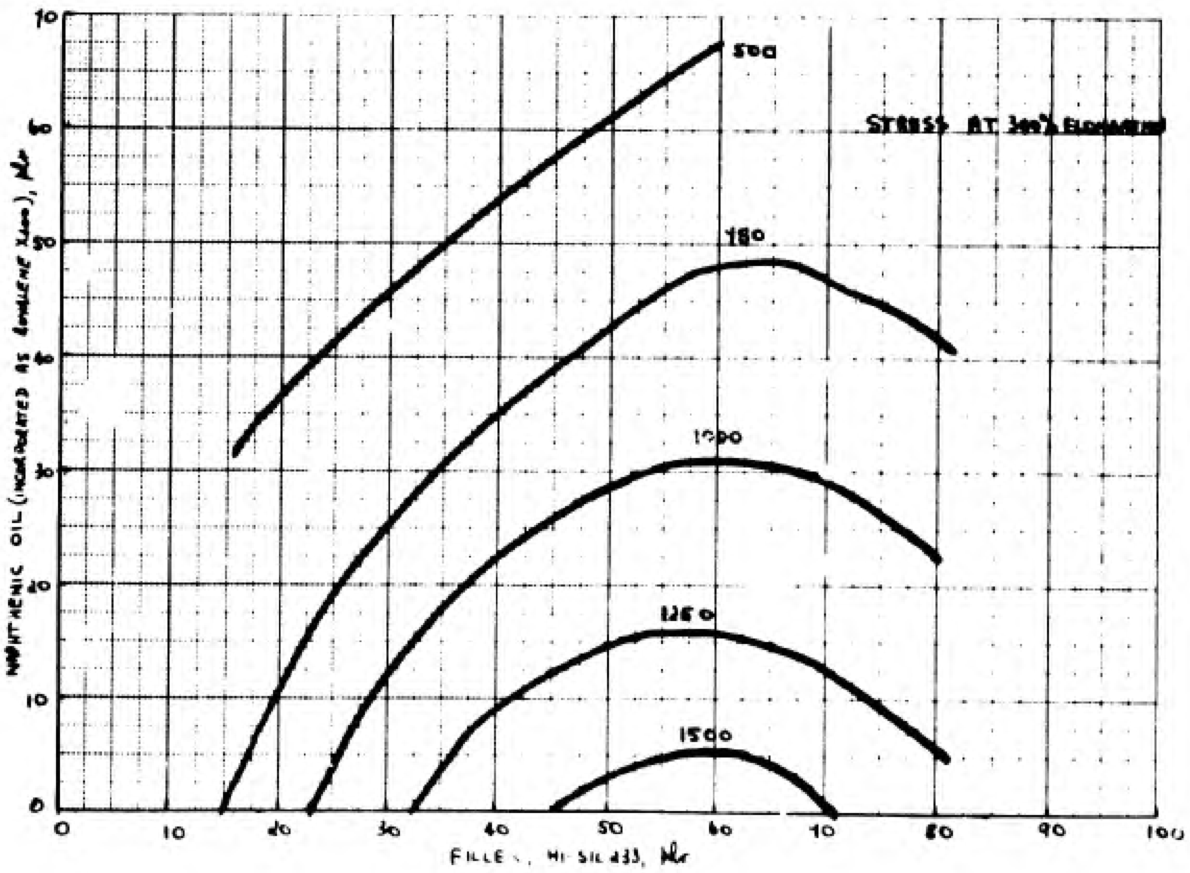

Figure 4c. Stress at 300% elongation of EPD rubbers at varying concentrations of silica and naphthenic oil

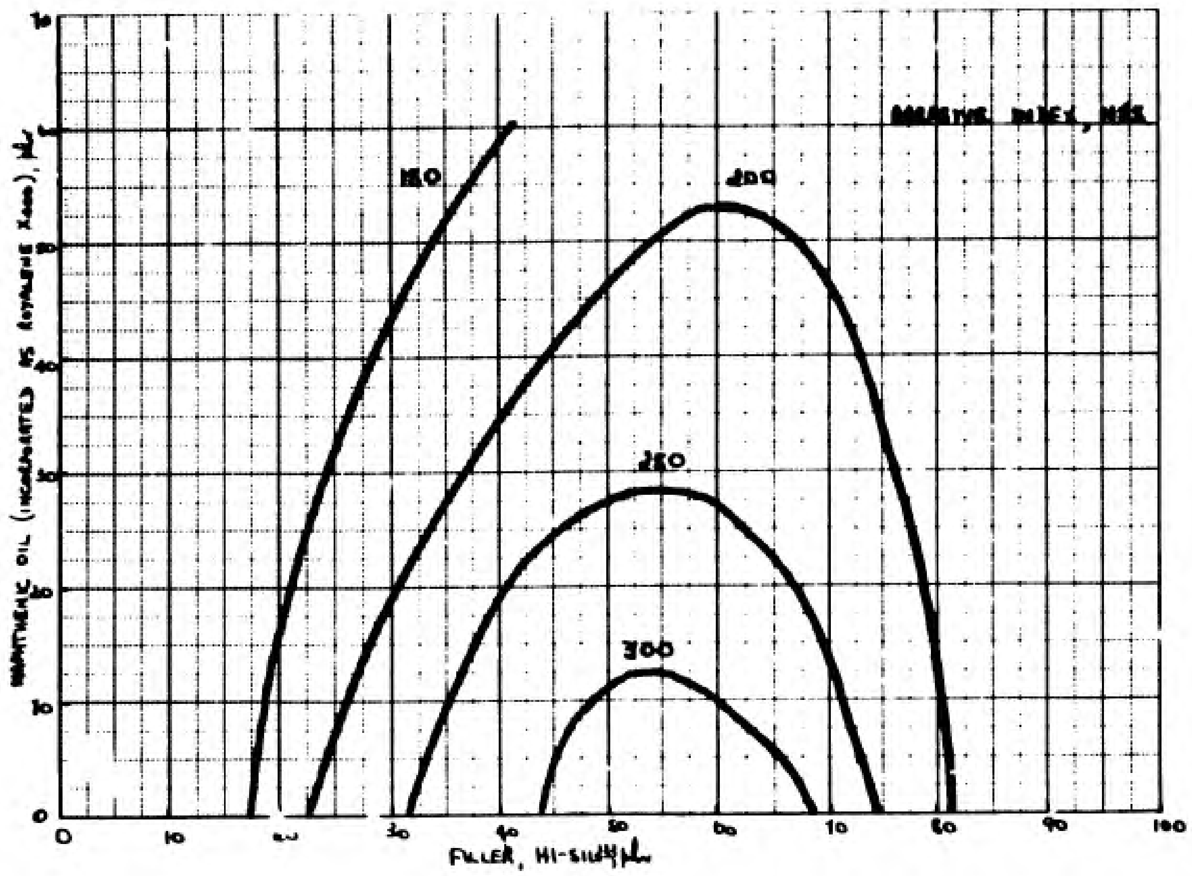

Figure 4d. Abrasive index, NBS, of EPD rubbers at varying concentrations of silica and naphthenic oil

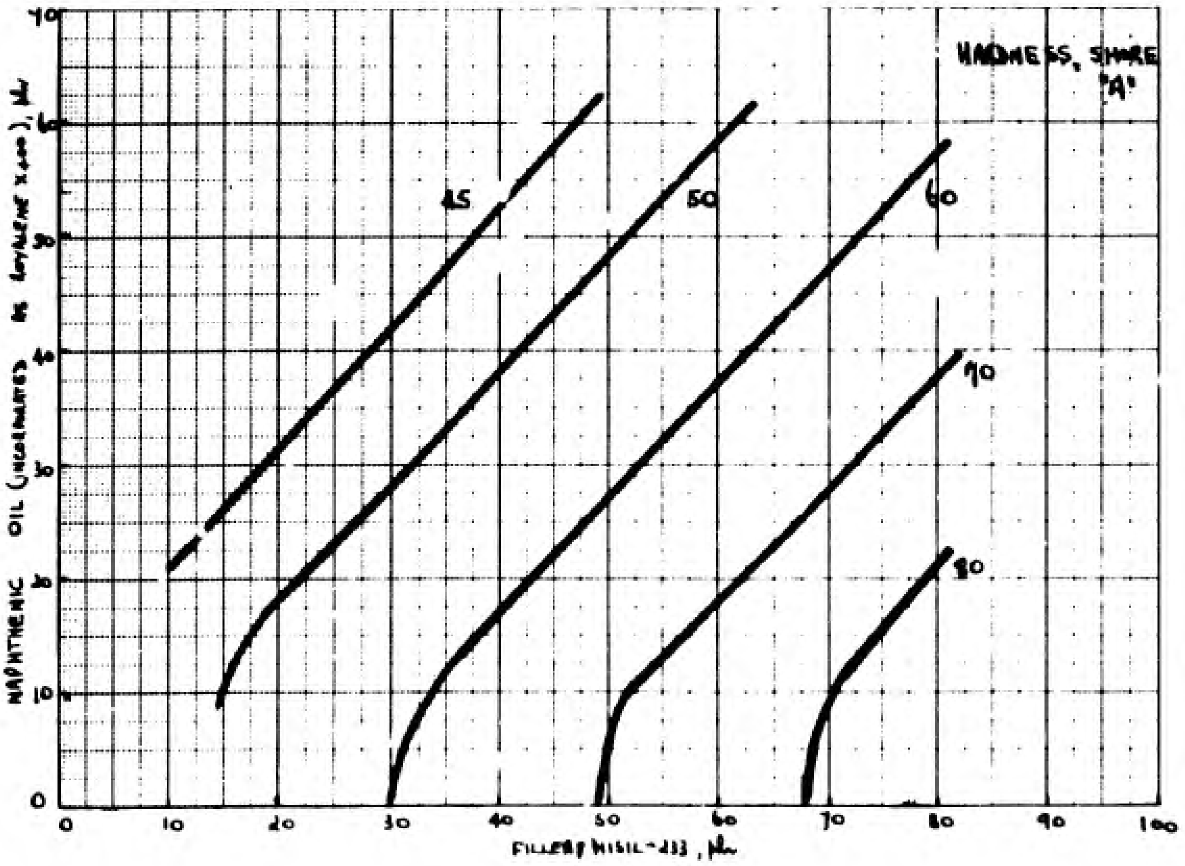

Figure 4e. Hardness, Shore A, of EPD rubbers at varying concentrations of silica and naphthenic oil

The presence of stearic acid is not essential for good vulcanization but small amounts (1 phr) improve processability and dispersion of the fillers, especially at high loadings. In the absence of stearic acid, there is no marked improvement in the physical properties of the EPD rubber vulcanizates.

5. Use of special additives

The rate of cure of mineral-filled EPD rubbers can be improved by the addition of polar rubbers such as chlorosulphonated polyethylene[22,36], or of other chlorine-containing compounds. Improvements are obtained in the scorch rate, compression set, permanent set, and stress at 300 percent elongation. The addition of chlorosulphonated polyethylene also gives vulcanizates with the maximum heat resistance, especially when used in conjunction with antimony trioxide[27] and high levels of zinc oxide[26]. In addition to covulcanizing with the EPD rubber, chlorosulphonated polyethylene is believed to give a large increase in the modulus due to reaction between the chlorine and chlorosulphonyl groups and the active groups on the surface of the silica filler.

The addition of chlorosulphonated polyethylene (7.5 phr) or octachlorocyclopentene (1.5 phr) to hot-milled silica-reinforced EPD rubber plasticized with either dioctyl sebacate or a naphthenic oil gives the maximum improvement in general physical properties. Chlorine-containing compounds, such as polychloroprene (7.5 phr), polyepichlorohydrin (7.5 phr), nitrile-polyvinylchloride resin blend (7.5 phr), p-toluene sulphonyl chloride (2.0 phr), hexachloroethane (2.0 phr), and dichlorodiphenyl-trichloroethane (2.0 phr), are not effective in improving the cure rate of silica-reinforced EPD rubbers. Perchloropentacyclodecane (7.5 phr), a known flame-proofing agent for ethylene-propylene copolymer rubber (EPR)[37], also has no effect on the cure rate.

Both chlorinated paraffin wax (7.5 phr) and tetrachloro-p-benzoquinone (2.0 phr) improve the rate of cure of silica-reinforced EPD rubbers but are not as effective as chlorosulphonated polyethylene or octachlorocyclopentene. These chlorine-containing additives are effective with both Nordel 1040 and Enjay 3509 EPD rubbers and give the maximum improvement in physical properties when used with hot-milled silica-reinforced compounds. The additives have no effect on the processing characteristics of EPD compounds, but both chlorosulphonated polyethylene and octachlorocyclopentene give improvements in the compression-set resistance of EPD rubbers at room temperature and at 100°C.

In the absence of a chemical promotor such as p-quinone dioxime, chlorosulphonated polyethylene (7.5 phr) or octachlorocyclopentene (1.5 phr) improves the physical properties of EPD rubbers and can be used for the

TABLE VI
PHYSICAL PROPERTIES OF EPD RUBBERS CONTAINING 50 PHR OF HI-SIL 233

Compound*	19	20	3	21	22	23	24
Nordel 1040 EPD rubber, phr	100	90	80	70	60	50	40
Royalene X400 EPD rubber, phr	0	20	40	60	80	100	120
Oil loading**, phr	0	10	20	30	40	50	60
Tensile strength, psi	3500	3450	3300	3250	3000	2750	2500
Ultimate elongation, %	500	520	540	600	620	640	700
Stress at 300% elongation, psi	1600	1350	1200	900	700	630	575
Hardness, Shore "A"	71	68	52	57	53	49	45
Abrasive index, NBS	310	310	275	225	200	175	165
Compression set after 24 hr at 100°C, %	71	71	71	71	71	74	74
Volume swell after 24 hr in ASTM, fuel B, R.T., %	117	110	105	101	97	95	92
Specific gravity	1.124	1.113	1.103	1.095	1.087	1.080	1.074
Mooney viscosity, ML(1/4), 121°C	114	90	76	69	66	65	64
Cost, cents/lb	26.4	25.4	24.4	23.6	22.9	22.2	21.6

*Formulation: Nordel 1040, Royalene X400 and plasticizer, as listed; Hi-Sil 233, 50; polyethylene glycol 4000, 1; stearic acid, 1; HAF black, 3; p-quinone dioxime, 1; chlorosulphonated polyethylene, 7.5. Compounds hot milled 10 min at 160°C.

Curing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. All compounds press cured 20 minutes at 160°C.

**Incorporated as Royalene X400 an oil-extended EPD rubber containing 100 phr of naphthenic oil.

TABLE VII

EFFECT OF MIXED FILLERS ON EPD RUBBERS

Compound*	25	26	27	28	29	30	31
Added filler, 25 phr	HAF black	Magnesium silicate	Kaolin hard clay	Calcium carbonate	Titanium dioxide	Antimony trioxide	Anhydrous silica
Tensile strength, psi	3100	2900	3100	2000	2300	2700	3600
Ultimate elongation, %	460	560	570	500	550	700	700
Stress at 300% elongation, psi	1600	950	1200	650	650	475	800
Hardness, Shore "A"	57	55	55	53	50	48	62
Abrasive index, NBS	265	109	137	84	153	138	249
Compression set, %, after							
24 hr at room temperature	5.7	4.8	5.0	4.3	4.2	7.3	11.9
24 hr at 100°C	67.5	70.4	65.1	67.2	64.0	65.0	74.4

*Formulation: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 25; polyethylene glycol, 0.5; stearic acid, 1. Added filler as listed, 25. Compounds hot milled 10 minutes at 160°C.

Curing system: zinc oxide, 5, sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. In compound 28, an extra 0.5 phr of polyethylene glycol was added before the hot-milling cycle. All compounds cured 20 minutes at 160°C.

TABLE VIII

CARBON BLACK REINFORCED EPD RUBBERS

Compound*	32**	33**	34**	35**
p-Quinone dioxime, phr	1	-	1	-
Time of hot milling	10'/160°C	Nil	10'/160°C	Nil
Curing system	Sulphur	Sulphur	Peroxide	Peroxide
Mooney properties at 138°C:				
Time to scorch, min (5 pts rise)	8.2	7.0	4.1	5.7
Minimum viscosity, points	60	50	61	50
Cure index, Δ 30, min	3.2	2.5	1.3	1.4
Mooney viscosity, ML(1+4), 121°C	70	62	66	57
Tensile strength, psi	2900	2500	2100	2050
Ultimate elongation, %	370	460	400	480
Stress at 300% elongation, psi	2300	1400	1250	1050
Hardness, Shore "A"	60	70	58	62
Abrasive index, NBS	440	240	1000+	600+
Compression set, %, after				
24 hr at room temperature	5.3	14.2	13.3	12.7
24 hr at 100°C	66.2	60.2	14.8	18.6
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	500	450	175	75

*Formulation: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; HAF black, 53; stearic acid, 1. p-Quinone dioxime and hot milling as listed.

Curing systems: sulphur type: zinc oxide 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5
peroxide type: dicumyl peroxide (40%), 9.0; trimethylolpropane trimethacrylate, 3.0

Compounds cured 20 minutes at 160°C.

**Equivalent silica-reinforced compounds:
32, Compound 3, hot milled
33, Compound 3, cold milled
34, Compound 10
35, Compound 9

compounds show good tensile strength, modulus, and abrasion resistance properties and poor cut-growth resistance. Their compression-set properties are similar to those of silica-reinforced compounds. Peroxide-cured carbon black reinforced compounds show superior physical properties as compared to sulphur-cured compounds and have excellent resistance to abrasion and compression set at elevated temperatures, and good cut-growth resistance. Cold-milled carbon black reinforced EPD rubbers have properties adequate for many applications, while hot milling improves certain properties but usually not to the same extent as it does for EPD rubbers reinforced with silica.

4. Blends of EPD rubbers with other elastomers

EPD rubbers are known to blend with other elastomers to give vulcanizates with improved ozone resistance. Sutton[39] has described the properties of some of these blends that are reinforced with carbon black. Oil-extended EPD rubber is very effective in improving the ozone resistance of silica-reinforced SBR compounds. For effective protection, the EPD rubber content should be at least 5 phr, and levels of 10 phr (20 phr for an oil-extended EPD rubber containing 100 phr of naphthenic oil) can be incorporated without markedly affecting the general physical properties of the vulcanizates.

Typical properties of SBR-EPD rubber blends are given in Table IX. Silica-reinforced SBR compounds cured with a conventional sulphur-accelerator system and with the zinc oxide level reduced to 1 phr have good physical properties and adequate resistance to heat aging at 70°C. As shown in Table IX, an antiozonant alone (3 phr, compound 37), or an EPD rubber alone (20 phr oil-extended compound 38), will not markedly improve the ozone resistance of an unprotected silica-reinforced SBR vulcanizate (compound 36).

The combined use of an antiozonant and an EPD rubber, however, gives vulcanizates (compound 39) with good physical properties and excellent ozone resistance. Carbon black reinforced SBR compounds may also be protected against ozone by this antiozonant-EPD rubber combination. The antiozonant N,N'-bis(1-methyl heptyl)-p-phenylenediamine (BMHPD, 3 phr), is very effective in silica-reinforced SBR compounds, although N,N'-bis(1,4 dimethyl pentyl)-p-phenylenediamine and N-isopropyl-N'-phenyl-p-phenylenediamine may also be used. The ozone resistance of the vulcanizates is not improved by the incorporation of sun-checking waxes (2 phr).

Silica-reinforced SBR-EPD rubber blends process easily and stearic acid lubricant is not required. Fast curing stocks are obtained by the use of triethanolamine activator (0.5 phr) with a resin softener (5 phr) to maintain the cut-growth resistance. Coumarone-indene resins, terpene-resin acid blends, and novolac-type and non-heat advancing phenolic resins are suitable. A typical vulcanizate with excellent ozone resistance is compound 40 (Table IX).

TABLE IX
BLENDS OF EPD RUBBER WITH SBR

Compound*	36	37	38	39**	40
Elastomer:					
Royalene X400***, phr	-	-	20	20	20
SBR 1502, phr	100	100	90	90	90
Light process oil, 10 phr	10	10	-	-	-
Antiozonant, 3 phr	-	BMHPD****	-	BMHPD	BMHPD
Mooney properties at 138°C:					
Time to scorch, min (5 pts rise)	11.1	9.3	9.5	8.7	7.3
Minimum viscosity, points	98	74	112	97	72
Cure index, Δ 30, min	4.1	2.1	3.3	2.6	1.6
Tensile strength, psi	2400	2500	2700	2700	2730
Ultimate elongation, %	600	650	570	620	670
Stress at 300% elongation, psi	800	670	900	800	700
Hardness, Shore "A"	63	63	66	65	66
Abrasive index, NBS	140	126	146	129	104
Cut growth after aging 24 hr at 100°C, 50,000 cycles, %	75	30	175	110	150
Ozone resistance, 50 pphm, 38°C	6				
Bent loop, time to crack, hr					
Unaged	6	12	6	1000+	1000+
Aged 70 hr at 70°C	6	6	6	1000+	1000+

*Formulation: Elastomer, process oil, antiozonant, as shown; Hi-Sil 233, 45; HAF black, 3; polymerized trimethyl dihydroquinoline, 1; zinc oxide, 1; benzothiazyl disulphide, 1.5; DOTG, 0.75; DPMTT, 0.5; sulphur, 3. In addition, compound 52 contains triethanolamine, 0.5; coumarone-indene resin (medium), 5. All compounds cured 15 minutes at 154°C.

**Compression set: 24 hr at room temperature, 6.3%; 24 hr at 100°C, 68.6%.

***An oil-extended EPD rubber containing 100 phr of naphthenic oil.

****N,N'-bis(1-methyl heptyl)-p-phenylene diamine.

Oil-extended EPD rubbers can also be blended with silica-reinforced blends of SBR and polybutadiene rubbers. Expanded vulcanizates of this type have excellent resistance to ozone and to abrasion.

D. Heat and Cold Resistance of EPD Rubbers

The saturated nature of the molecular backbone and the low concentration of pendant unsaturation enables general purpose EPD rubbers to be serviceable at 120°C, while special compounding permits long term service at 150°C [8,9,26]. Although carbon black reinforced compounds have superior heat resistance to mineral-filled compounds, the use of silica in EPD rubbers gives vulcanizates with a heat resistance adequate for many applications. Where maximum heat resistance is required, perioxide curing systems should be used.

Compounds processed by hot milling have superior physical properties and are less sensitive to heat aging than cold-milled compounds. Hot-milled compounds, heat aged at 100°C for 7 days, show a slight reduction in tensile strength and ultimate elongation and a hardness increase of several points. Heat aging for from 16 to 24 hours at 100°C is a convenient method of improving the modulus and compression-set characteristics of silica-reinforced EPD rubbers. The properties of cold-milled EPD rubbers can also be greatly improved after molding by an oven cure of up to 72 hours at 100°C.

For many military applications of rubber, flexibility at low temperatures is required. EPD rubbers do not crystallize at low temperatures and high quality compounds are reported[9] to remain flexible down to from -50°C to -60°C and to have brittleness temperatures as low as -70°C.

Tests carried out on hot-milled silica-reinforced EPD rubbers plasticized with 20 phr of di-2-ethyl hexyl sebacate indicate that the limit of low-temperature serviceability, as assessed by the Gehman T5 value, is about -58°C. Compounds containing naphthenic oil plasticizers or blends of these and di-2-ethyl hexyl sebacate are less flexible at low temperatures. The Gehman low-temperature values and the temperature of retraction values of two EPD rubbers are given in Table X. Compounds plasticized with tri-2-ethyl hexyl phosphate exhibit low-temperature properties similar to compounds plasticized with di-2-ethyl hexyl sebacate.

Recently, Wilson[40] has shown that hot-milled sulphur-cured EPD rubbers have better low-temperature flexibility than hot milled, peroxide-cured rubbers, and both are superior to cold-milled compounds. Vulcanizates reinforced with silica have low-temperature properties similar to compounds reinforced with HAF carbon black.

TABLE X

LOW TEMPERATURE PROPERTIES OF EPD RUBBERS

Compound	1*	3*
Plasticizer, phr	Dioctyl sebacate, 20	Naphthenic oil, 20
Gehman low temperature stiffness, °C.		
T_2	-46	-28
T_5	-58	-48
T_{10}	-62	-51
T_{100}	Below -65	-60
Low temperature retraction, °C		
TR10	-55	-46
TR30	-49	-39
TR50	-43	-33
TR70	-35	-26

*See Table II

E. Ozone, Chemical, Fungal, and Weather Resistance of EPD Rubbers

Properly compounded carbon black reinforced EPD rubbers have excellent ozone resistance[8,9,10]. Stressed silica-reinforced EPD rubber vulcanizates also show excellent ozone resistance and no signs of cracking after exposure at 38°C to an ozone concentration of 50 pphm for 1000 hours.

The vulcanizates have good resistance to such polar materials as water, phosphate esters, and glycols, as well as to many acids and alkalies, but swell considerably in aliphatic and aromatic solvents, chlorinated hydrocarbons, and certain mineral oils. The volume-swell characteristics of a range of silica-reinforced vulcanizates are given in Table VI.

The U. S. Army has a continuing need for fungal-resistant rubbers to be used for molded components, footwear, coated fabrics, and is evaluating the effects of commonly used fungicides on various rubbers[41]. Black and non-black EPD rubbers, plasticized with naphthenic oils (20 phr) and crosslinked with accelerators based on tetramethylthiuram disulphide and 2-mercaptobenzothiazole, have excellent fungal resistance. Vulcanizates show no fungal growth after tests in the laboratory or after exposure in a tropical test chamber. Phosphate and phthalate ester plasticizers with good antifungal properties[42] may also be used in EPD rubbers.

Although copper 8-hydroxy quinolinolate will improve the cure rate of silica-reinforced EPD rubbers, its presence is not required to ensure adequate fungal resistance of the vulcanizates. EPD rubbers show good resistance to fungi during soil burial tests. Black and non-black vulcanizates exposed for eight weeks and tested at two weekly intervals show good retention of general physical properties. Water leaching of vulcanizates before soil burial does not markedly affect their physical properties or their fungal resistance. Details are given in Table XI.

EPD rubber vulcanizates, unless protected by a screening agent such as carbon black or titanium dioxide, are very sensitive to deterioration by ultraviolet light. As shown in Table XI (compounds 41,42), unprotected vulcanizates are seriously degraded after exposure to ultraviolet light for 100 hours, while vulcanizates containing carbon black, 3 phr, (compound 3) show good retention of physical properties.

In the absence of screening compounds, both Nordel 1040 and Enjay 3509 vulcanizates are seriously degraded by ultraviolet light. For adequate protection, they require carbon black or combinations of color pigments and titanium dioxide.

Properly compounded silica-reinforced EPD rubbers possess good weathering characteristics. As shown in Table XII, black, olive drab, and white compounds showed adequate retention of physical properties and no surface deterioration after outdoor exposure at Natick for 6 months. Red compounds (iron oxide pigment), 6 phr, and dark gray compounds (titanium dioxide and fine thermal black, 5:1), 6 phr, as well as vulcanizates heat aged for 16 hours at 100°C were also found to possess good weathering resistance.

TABLE XI

FUNGAL RESISTANCE OF EPD RUBBERS

Compound*	3	41	42
Elastomer, 80 phr	Nordel 1040	Enjay 3509	Enjay 3509
Fungicide, 0.5 phr	Nil	Nil	Cu8-hydroxy quinolinolate
Activator, 1 phr	p-Quinone dioxime	TETD	TETD
Carbon black, phr	3	-	-
Fungal resistance, ASTM1924-61T, 40 days exposure	No growth	No growth	No growth
Tropic chamber exposure, 30°C, 87-92% R.H., 90 days	No growth	No growth	No growth
Physical properties, as molded, unaged:			
Tensile strength, psi	3400	4000	2850
Ultimate elongation, %	560	620	520
Stress at 300% elongation, psi	1150	1100	1250
Hardness, Shore "A"	61	67	67
Physical properties, after soil burial for 8 weeks			
Tensile strength, psi	3200	3350	2900
Ultimate elongation, %	620	570	540
Stress at 300% elongation, psi	900	1000	1000
Hardness, Shore "A"	63	69	69
Physical properties, as molded, after 100-hr weatherometer exposure			
Tensile strength, psi	3100	1000	1350
Ultimate elongation, %	550	280	310
Stress at 300% elongation, psi	1200	-	1300
Hardness, Shore "A"	63	68	68
Physical properties after 100 hr weatherometer exposure and soil burial for 8 weeks			
Tensile strength, psi	2800	1000	1450
Ultimate elongation, %	600	300	350
Stress at 300% elongation, psi	900	1000	1100
Hardness, Shore "A"	63	69	69

*Formulations: Compound 3, see Table II. Compounds 41, 42: Enjay 3509, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; Hi-Sil 233, 50; polyethylene glycol, 1; stearic acid, 1; TETD, 1; zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5. Fungicide as listed. All ingredients milled on cold mill. Stock then hot milled 10 min at 121°C. All compounds cured 20 min at 160°C. Rubbers required for fungal testing were molded in a chrome-plated mold (6 x 6 x 0.075 inches) with no mold lubricant.

TABLE XII
WEATHER RESISTANCE OF EPD RUBBERS

Compound*	Color	Physical Properties	Period of outdoor exposure at Natick**		
			Nil (as molded)	3 months	6 months
3	Black	Tensile strength, psi	3500	3500	3200
		Ultimate elongation, %	540	550	480
		Stress at 300% elongation, psi	1225	1300	1650
		Hardness, Shore "A"	59	61	66
43	Olive drab	Tensile strength, psi	3550	2900	2600
		Ultimate elongation, %	560	560	470
		Stress at 300% elongation, psi	1000	1000	1350
		Hardness, Shore "A"	59	61	63
44	White	Tensile strength, psi	3300	2350	2350
		Ultimate elongation, %	640	600	540
		Stress at 300% elongation, psi	575	600	800
		Hardness, Shore "A"	56	60	64

*Formulations: Compound 3, see Table II. Compound 43, same as compound 3 but with the HAF black (3 phr) replaced by olive drab pigment (8 phr) consisting of: chrome green, 85.5%; red iron oxide, 12.5%; fine thermal black, 2.0% by weight. Compound 44, Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; stearic acid, 1; polyethylene glycol 1; Hi-Sil 233, 42. Compounds hot milled 10 min at 160°C.

Curing system and pigment: zinc oxide, 5; sulphur 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5; titanium dioxide, 14. All compounds cured 20 min at 160°C.

**Exposure commenced 1 October 1964.

F. Expanded Silica-Reinforced EPD Rubbers

Silica-reinforced EPD rubbers may be expanded with chemical blowing agents such as N,N-dinitrosopentamethylenetetramine (40%), azodicarbonamide, or p,p'-oxybis-(benzenesulphonylhydrazide), although the latter can cause some retardation of the curing system. The use of a surface-coated urea promotor with any of the blowing agents will eliminate unpleasant odors. To develop expanded rubbers with uniform cell structure, close control of the plasticity as determined by the silica and oil loading is required.

In silica-reinforced EPD rubbers, a press cure of 7 minutes at 160°C will give the required degree of expansion but the rubber in the cell walls will not have sufficient strength to prevent collapse of the cell network. A press cure of 15 minutes at 160°C, followed by an oven cure of 30 minutes at 160°C, gives expanded rubbers with good physical properties. Typical results for two expanded rubbers of differing densities are given in Table XIII.

Expanded silica-reinforced EPD rubbers have good tear, abrasion, compression-set, and dynamic-recovery properties. They also have good water resistance. Their oil resistance may be controlled, to some extent, by the plasticizer loading[43]. They can be made in a wide range of densities and colors using conventional processing equipment and techniques. Their ability to accept large amounts of compounding oils and their excellent ozone and weather resistance enables them to be blended with other elastomers such as butyl rubber to give products with excellent shock-absorbing properties[43]. Spenadel and coworkers[43,44], describe the use of expanded EPD rubber in automotive sponge applications and Machado[45] its use in shoe soling.

V. Military Potential of EPD Rubbers

For military use, general-purpose rubbers must have good resistance to heat aging, weathering, ozone, abrasion, compression set, and attack by chemicals and must be serviceable over the temperature range of from -50°C to +150°C. Suitably compounded EPD rubbers meet each of these requirements.

Either carbon black or silica-reinforced EPD rubbers should be suitable for such applications as tank track pads, gaskets and seals for ammunition boxes and other ordnance and electrical equipment, weatherstripping, miscellaneous vehicle components, and soling for military footwear. Their excellent electrical properties[46] could be used to advantage in the insulant and outer jacketing of military cables for arctic and tropical use. Their good low-temperature, heat, and abrasion properties suggest their use in heavy duty, off-the-road military tires[47].

TABLE XIII

EXPANDED SILICA-REINFORCED EPD RUBBERS

Compound*	45	46
N,N-dinitrosopentamethylenetetramine (40%)	5.0	7.5
Surface-coated urea promotor	1.5	2.25
Mooney properties at 138°C:		
Time to scorch, min (5 pts rise)	11.0	11.0
Minimum viscosity, points	44	44
Cure index, Δ 30, min	2.8	2.9
Mooney viscosity, ML(1+4), 121°C	64	67
Properties** of molded test sheet:		
Tear strength, pounds per inch	154	108
Tensile strength, psi	1200	950
Ultimate elongation, %	510	510
Stress at 300% elongation	450	350
Hardness, Shore "A"	55	45
Properties*** of a molded test slab:		
Density, lb/ft^3	27.7	17.8
Compression deflection, psi (25% deflection)	21.6	12.6
Compression set, % (24 hr at 70°C)	59.3	73.2
Water absorption, %	1.30	2.59
Recovery properties, sec****	1	1

*Formulation: Nordel 1040, 80; Royalene X400, 40; chlorosulphonated polyethylene, 7.5; HAF black, 3; Hi-Sil 233, 50; p-quinone dioxime, 1; polyethylene glycol, 1; stearic acid, 1. Compounds hot milled 10 min at 160°C. Curing and blowing system: zinc oxide, 5; sulphur, 2; TMTD, 0.75; DPMTT, 0.75; MBT, 1.5; blowing agent and blowing promotor as listed; petroleum jelly, 5. Compounds press-cured 15 min at 160°C, followed by an oven cure for 30 min at 160°C. In all cases, a mold loading of 85% nominal capacity was used.

**From a 6 x 6 x 0.75 inch mold.

***From a 3 x 3 x 0.50 inch mold.

****Ref 43. Rating: 1 sec or less, good;
1.5 sec or more, poor.

Their excellent resistance to polar liquids, phosphate ester-based plasticizers and fluids, and isopropyl nitrate propellants[48] indicates that they could be used for seals and gaskets that are in contact with these materials. These rubbers also have dynamic applications[49].

Synthetic fabrics coated with EPD rubber should be suitable for ponchos, foul weather clothing, heavy duty truck and gun covers, and inflated structures such as airhouses and liferafts. Expanded EPD rubbers, which are characterized by good shock-absorbing and thermal-insulating properties, should find applications in military packaging and in cold weather clothing and footwear.

VI. Conclusions

Hydrated silica is an effective, low-cost, non-black, reinforcing filler for the amorphous ethylene-propylene diene rubbers at present available in the United States. High quality vulcanizates can be produced in all colors by suitable compounding. To obtain optimum vulcanizate properties it is necessary to hot mill the rubber and the silica in the presence of chemical promotors and silica activators. The rubbers may be crosslinked with either peroxide or sulphur curing systems.

Properly compounded silica-reinforced EPD rubber vulcanizates are usable over a temperature range of from -50°C to +150°C and have excellent resistance to ozone, heat aging, weathering, and fungal and chemical attack. They are not oil-resistant. Expanded silica-reinforced EPD rubbers with good physical properties can be produced by conventional processing techniques.

VII. Recommendations

The attractive properties of carbon black or silica-reinforced EPD rubbers warrant their investigation for many of the military applications described in Section V. Typical high quality vulcanizates should be examined to determine the applicability to them of the latest military standard on vulcanized rubber[50].

Because compounding has a marked effect on the weather resistance of EPD rubbers, there should be further outdoor exposures of black and non-black vulcanizates under temperate, desert, and tropical environments. The low-temperature properties of these rubbers should also be further studied by means of the new low-temperature testing techniques being developed by Wilson[40]. In addition, studies should be conducted on heat-curable and pressure-sensitive adhesives for EPD rubbers.

VIII. Acknowledgments

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APPENDIX I

Compounding Materials

Material	Trade Name	Supplier No.*
Anhydrous silica	Carb-O-Sil	3
Antimony trioxide	-	14
Azodicarbonamide	Celogen AZ	16
Benzothiazyl disulphide	Altax	32
Bis (hydroxymethyl) 1,4 cyclohexane	-	6
Calcium carbonate	Camel-WITE	9
Carbon black, fine thermal	P33 black	32
Carbon black, HAF	Philblack O	20
Chlorinated paraffin wax	Chlorowax 70	4
Chlorosulphonated polyethylene	Hypalon 40	5
Copper dimethyldithiocarbamate	Cumate	32
Copper-8-hydroxy quinolinolate	Milmer No. 1	18
Coumarone-indene resin (medium soft)	Neville R-15	17
Coumarone-indene resin (medium)	Cumar MH-1	1
Dibenzo-p-quinone dioxime	Dibenzo GMF	16
Dichlorodiphenyltrichloroethane	DDT	6
Dicumyl peroxide (40% active)	Dicup 40C	10
Di-2-ethylhexyl adipate	Flexol DOA	28
Di-2-ethylhexyl phthalate	Flexol DOP	28
Di-2-ethylhexyl sebacate	Flexol DOS	28
Di-orthotolylguanidine	DOTG	5

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*See Appendix II

Material	Trade Name	Supplier No.*
Dipentamethylenethiuram tetrasulphide	DPMTT, Tetrone A	5
Diphenylguanidene	DPG	13
4,4'-Dithiodimorpholine	DTDM, Sulfasan R	13
Ethyleneglycol dimethacrylate	SR 206	22
Ethylene-propylene diene rubber (EPDR)	Nordel 1040	5
Ethylene-propylene diene rubber (EPDR)	Enjay 3509	7
Ethylene-propylene diene rubber, oil extended (EPDR)	Royalene X400	16
Hexachloroethane	-	6
Hexamethoxymethyl melamine	HMMM, Cymel 300	2
Hydrated aluminum silicate	Paragon clay	12
Hydrated silica	Hi-Sil 233	21
Kaolin hard clay	Dixie clay	32
Magnesium silicate	Mistron Vapor	24
2-Mercaptobenzothiazole	MBT, Captax	32
Methylated tall oil ester	Metalyn 100	10
Mixture of selected waxes	Sunproof Jr.	16
Naphthenic oil (light colored)	Light process oil	25
N,N'-bis (1,4 dimethylpentyl)-p-phenylenediamine	Eastozone 33	6
N,N'-bis (1-methylheptyl)-p-phenylenediamine	UOP88	30
N,N-dinitrosopentamethylenetetramine (40% active)	Unicel ND	5
N-isopropyl-N'-phenyl-p-phenylenediamine	Flexzone 3-C	16

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* See Appendix II

Material	Trade Name	Supplier No.*
N-Me-N4 dinitrosoanilene (33% active)	MDNA, Elastopar	13
Nitrile-polyvinylchloride resin blend	Paracril Ozo	16
Novolac-type phenolic resin	Schenectady SP8014	23
Octachlorocyclopentene	C58	11
p,p'-Oxybis-(benzenesulphonylhydrazide)	Celogen	16
Paraffinic oil plasticizer	Circosol 551	25
Pentaerythritol 200	-	10
Perchloropentacyclodecane	Declorane	11
Petroleum jelly	Pureline Petrolatum	19
Phenolic resin (non-heat advancing)	Bakelite CRR0909	28
Polyalkanolpolyamine	Nalco L-1718	15
Polychloroprene	Neoprene WRT	5
Polyepichlorohydrin	Hycar CHR	8
Polyether plasticizer	TP-110	26
Polyethylene glycol	Carbowax 4000	28
Polymerized trimethyl dihydroquinoline	Agerite Resin D	32
Polymethylpolyphenylisocyanate	PAPI	31
p-Quinone dioxime	GMF	16
SBR 1502	Philprene 1502	20
Selenium dimethyldithiocarbamate	Methyl Selenac	32
Surface-coated urea	BIK	16
Tellurium diethyldithiocarbamate	Ethyl Tellurac	32
Terpene-resin acid blend	Turgum S	12

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*See Appendix II

Material	Trade Name	Supplier No.*
Tetrachloro-p-benzoquinone	Vulklor	16
Tetraethylthiuram disulphide	TETD, Thiuram E	5
Tetramethylthiuram disulphide	TMTD, Methyl Tuads	32
Titanium dioxide	Titanox RA40	27
p-Toluene sulphonyl chloride	-	6
Triallyl cyanurate	TAC	2
Tri (2-ethylhexyl) phosphate	Flexol TOF	28
Trimethylolpropane trimethacrylate	SR350	22
Vinyl coated silica	Santocel C (vinyl coated)	29
Zinc dimethyldithiocarbamate	ZDC, Methazate	16

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*See Appendix II

APPENDIX II

Material Suppliers

No.

1. Allied Chemical Corp., Philadelphia, Pa.
2. American Cyanamid Co., Bound Brook, N.J.
3. Cabot Corp., Boston, Mass.
4. Diamond Alkali Co., Cleveland, O.
5. E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
6. Eastman Chemical Products, Kingsport, Tenn.
7. Enjay Chemical Co., Linden, N.J.
8. B. F. Goodrich Chemical Co., Cleveland, O.
9. Harry T. Campbell Sons Corp., Towson, Md.
10. Hercules Powder Co., Wilmington, Del.
11. Hooker Chemical Co., Niagara Falls, N.Y.
12. J. M. Huber Corp., New York, N.Y.
13. Monsanto Chemical Co., Akron, O.
14. M and T Chemical Co., Rahway, N.J.
15. Nalco Chemical Co., Chicago, Ill.
16. Naugatuck Chemical Co., Naugatuck, Conn.
17. Neville Chemical Co., Pittsburgh, Pa.
18. Nuodex Products Co., Elizabeth, N.J.
19. Oils, Inc., Patterson, N.J.
20. Phillips Chemical Co. (Rubber Chemicals Div.), Akron, O.
21. Pittsburgh Plate Glass Co., Pittsburgh, Pa.
22. Sartomer Resins, Inc., Philadelphia, Pa.

No.

23. Schenectady Varnish Co., Inc., Schenectady, N.Y.

24. Sierra Talc and Clay Co., South Pasadena, Calif.

25. Sun Oil Co., Philadelphia, Pa.

26. Thiokol Chemical Corp., Trenton, N.J.

27. Titanium Pigment Corp., New York, N.Y.

28. Union Carbide Corp., New York, N.Y.

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30. Universal Oil Products, Des Plaines, Ill.

31. Upjohn Co., Kalamazoo, Mich.

32. R. T. Vanderbilt Co., Inc., New York, N.Y.

APPENDIX III

Standard Test Methods

Federal Test Method Std. No. 601	Method Number
Tensile Strength	4111
Ultimate elongation	4121
Stress at 300% elongation	4131
Hardness	3021
Volume swell	6211
Specific gravity	14011
Federal Test Method CCC-T-191b	
Accelerated weatherometer exposure	5670
Soil burial resistance	5762
Water leaching resistance	5830
A.S.T.M. Standards	**ASTM Designation**
Abrasion resistance, NBS	1630
Compression-set resistance	395
Cut-growth resistance	1052
Fungal resistance	1924
Gehman low-temperature stiffness	1053
Expanded cellular rubber properties	1056
Low-temperature retraction	1329
Mooney viscosity, scorch and cure index	1646
Ozone resistance	1149
Tear resistance (die "C")	624
Test sheet preparation	15
Weathering resistance	518

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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U. S. Army Natick Laboratories

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SILICA-REINFORCED ETHYLENE-PROPYLENE DIENE (EPD) RUBBERS

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5 AUTHOR(S) *(Last name, first name, initial)*
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11 SUPPLEMENTARY NOTES

12 SPONSORING MILITARY ACTIVITY
Rubber, Plastics & Leather Engineering Br., Clothing & Organic Materials Div., U. S. Army Natick Laboratories, Natick, Mass. 01762

13 ABSTRACT

High quality ethylene-propylene diene (EPD) rubber vulcanizates can be produced by using hydrated silica as the reinforcing filler. Modification of EPD rubber by chemical promotors such as p-quinone dioxime and the use of silica activators such as polyethylene glycol gives compounds with an acceptable rate of cure. Hot mastication, especially in the presence of halogenated compounds, gives vulcanizates with good physical properties. Processing aids such as stearic acid may be used, and oil-extended EPD rubber is a convenient plasticizer for silica-reinforced compounds.

To reduce costs, silica fillers can be extended with other such low-cost fillers as hard clay. EPD rubbers may also be blended with other elastomers. High quality silica-reinforced expanded EPD rubbers may be produced by conventional blowing agents and processing techniques. Silica-reinforced EPD rubbers crosslinked with organic peroxides give vulcanizates with good resistance to abrasion and compression set.

EPD rubber vulcanizates have excellent resistance to ozone and fungi and, in the presence of ultraviolet screening agents, show good weathering properties. It is expected that, in the future, ethylene-propylene diene rubbers will have many applications in military equipment.

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Unclassified
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Preparation (Formulation)	8					
EPD Rubbers	1		1,2		1	
Minerals	1					
Fillers	1					
Vulcanizates	2		2			
Armed Forces Supplies	4					
Reinforcement			8			
Silica			1			
Hydrated			0			
Carbon Black			1			
Curing					8	
Sulfur Systems					10	
Peroxide Systems					10	
Metal-containing Dithiocarbamates					5	

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