CENTRAL RESEARCH LABORATORY

DEVELOPMENT OF FIRE RETARDANT ELASTOMERS
Final Report
Research and Development Command
Contract No. DA-19-129-QM-841
QM Project No. 7-93-15-004

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DEVELOPMENT OF FIRE RETARDANT ELASTOMERS.

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Quartermaster Research and Development
Command

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~~Central Research Laboratory~~
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FOREWORD

This report, covering the research under Contract No. DA 19-129-QM-841, QM Project No. 7-93-15-004, titled "Development of Fire Retardant Elastomers," was carried out at the Central Research Laboratory of The Borden Chemical Company, a division of The Borden Company, for the Quartermaster Research and Development Command by Dr. Wolf Karo assisted by Messrs. H. Keuchel, J. L. McCorkle, and D. Kuhn.

The period covered by this report is from June 1959 to March 31, 1960.

The advisory assistance of Dr. B. David Halpern and Dr. Helmuth L. Pfluger in carrying out this research, is gratefully acknowledged.

<u>TABLE OF CONTENTS</u>

INTRODUCTION

Purpose:

The purpose of this contract is the development of elastomeric materials which have high resistance to very high temperatures, to fire, or to thermal radiation. These elastomers are also to remain flexible at low temperatures. The products to be developed are to be useful for the stated purpose both by themselves and as coating or impregnating materials for various fabrics, particularly Nylon and Fortisan.

General:

The major effort of research under this contract was devoted to the emulsion copolymerization of elastomeric monomers (isoprene, chloroprene, acrylates, with flame-retardant olefinic compounds such as:

bis(2-chloroethyl) vinylphosphonate	(CVP),
diallyl allylphosphonate	(DAAP),
diallyl chloromethylphosphonate	(DACP),
diallyl phenylphosphate	,
hexachlorobutadiene	(HCBD),
and phenyl allyl allylphosphonate	(PAAP),

Other monomers such as acrylonitrile and vinylidene chloride were also incorporated into several compositions. Copolymers of elastomeric monomers with diallyl chloromethylphosphonate or with vinylidene chloride were self-extinguishing (Q.M. number of 4). The incorporation of a low molecular weight polymer of CVP into an Acrylon Rubber by milling also produced a self-extinguishing elastomer. The other flame-retardants listed, did not produce permanently non-flammable copolymers. In several cases, no true copolymers were produced. For example, attempts to copolymerize HCBD with a number of monomers led to polymeric products from which the HCBD could be extracted.

The self-extinguishing characteristics of Neoprene were not improved by milling low molecular weight CVP into it.

DISCUSSION

A major portion of the research carried out under this contract has been devoted to a study of copolymerization of elastomeric monomers with monomers which were expected to confer flame retardance. Among the latter, bis(2-chloroethyl) vinylphosphonate (CVP) with a 13.3% phosphorus and 30.5% chlorine content and hexachlorobutadiene with an 81.6% chlorine content seemed particularly promising. Other phosphorus-containing monomers considered were: diallyl allylphosphonate, diallyl chloromethylphosphonate, diallyl phenylphosphate, and phenyl allyl allylphosphonate.

The preliminary preparations indicated that isoprene based materials prepared with hexa chlorobutadiene (HCBD) and with phenyl allyl allylphosphonate (PAAP) had desirable volume swells and torsional moduli as tested at the Contractor's laboratories, whereas materials containing CVP with and without acrylonitrile were of lesser interest (Table I).

The difference in flame-retardance observed on these samples between the QM laboratories and our laboratory was attributed in part to a slight difference in testing technique.

Table I

Test Data on Elastomers Submitted to QM September 4, 1959
as Returned by QM September 21, 1959

Sample No. 75-37-	Initial Charge (Weight %)	Fire-Retardancy		Flexibility Temperatures (°C)				*** Volume Swell	Tortional Modulus (psi)
		Borden	QM R & E	T_2	T_5	T_{10}	T_{100}		
65	15% CVP, 85% Ip	4	1	4.5*	-10.5	-21.0	-44.0	406	17
66	" " " "	5	2 - 3	6.5*	- 7.5	-25.0	-48.5	208	45
67	" " " "	4	2	17.0*	5.5	-3.5	-27	304	42
68	4.5% CVP, 4.5% AN, 91% Ip	4	1	13.0*	-1.0	-9.0	-23.0	178	138
69	" " 8.0% AN, 87.5% Ip	4	2	13.5*	1.5	-7.0	-23.0	355	19
70	8.5% CVP, 15.0% AN, 76.5% Ip	4	1 - 2	15.0*	6.3	0.0	-15.0	272	25
71	14.8% CVP, 27.0% AN, 58.2% Ip	4	1 - 2	18.0*	12.0	8.0	-2.5	61	18
72	30% CVP, 55% AN, 15% Ip	4	2 - 3	23.0**	18.5	15.0	6.0	6.4	197
73	40% CVP, 30% AN, 30% Ip	4	2	19.0**	13.0	10.0	6.0	18.6	297
74	Chloroprene latex treated with CVP	5	5	18.5*	-26.0	-29.5	-37.0	14.7	49
75	10.0% Hexachlorobutadiene, 90.0% Ip	5	4	16.0*	3.0	-5.0	-36.5	364	19
76	20.0% Hexachlorobutadiene, 80.0% Ip	5	2	22.0*	15.0	6.0	-22.	353	20
77	10.0% Phenylallyl Allylphosphonate + 90% Ip	5	1	22.0*	17.0	13.0	1.0	330	21
78	20.0% Phenylallyl Allylphosphonate + 80% Ip	5	3 - 4	21.0*	13.5	9.5	-13.0	214	24

*Black wire; **White wire; *** Fluid No. 2 (60% Isooctane; 5% benzene; 20% toluene; 15% xylene).

However, chlorine analysis of isoprene polymers prepared with HCBD feeds of 10 and 20% respectively indicated compositions of 0.53 and 1.04% of HCBD respectively. Increasing the feed of HCBD to 80% resulted in an isoprene polymer containing only 4% HCBD by chlorine analysis. Retesting of these elastomers for flame retardance showed a decreased flame retardance on aging. Retesting of virtually all of the polymers submitted to QM up to that time indicated a decrease in flame retardance. This lowering of the flame-retardance was therefore attributed to residues of trapped flammable solvents or monomers, gradual formation of flammable compounds by degradation, as well as slow migration of fire-retardant monomer.

Table II shows some of the changes in flame retardance observed with time.

Careful work-up of the coagulating solvent used in a repeat preparation of isoprene-HCBD copolymer indicated that essentially all of the hexachlorobutadiene was extracted by the solvent. Therefore, it is postulated that no copolymerization had taken place.

Copolymers of isoprene, ethyl acrylate, or butyl acrylate and diallyl chloromethylphosphonate were self-extinguishing. Since the phosphonate monomer is ignitable the residual monomer has to be carefully removed with cold alcohol extractions. Upon prolonged heating of the polymers at 110°C, flame retardance is reduced. Furthermore, upon exhaustive extraction of the polymer with an alcohol in a Soxhlet extractor, the flame retardance was reduced. Probably, this extensive treatment with isopropanol, in effect, removed the flame-retardant moiety by transesterification with the formation of a simple chloromethylphosphonate ester of the extracting alcohol.

Table II

Change of Flame Retardance With Time

Sample No. 75-37-	Composition of Monomer Feed (Weight per cent)	Flame Retardance 8/31/59	10/28/59	After Milling 10/26/59	% Chlorine Found Retained Sample	Milled at QMC	Av.	% HCBD in Polymer
65	15% CVP - 85% Ip	4	5	4				
66	" " " "	5	3	2				
67	" " " "	4	4	1				
68	4.5 CVP-4.5 AN-91 Ip	4	1					
69	4.5 CVP-8.0 AN-87.5 Ip	4	1					
70	8.5 CVP-15.0 AN-76.5 Ip	4	2					
71	14.8 CVP-27 AN-58.2 Ip	4	2					
72	30 CVP-55 AN-15 Ip	4	1					
73	40 CVP-30 AN-30 Ip	4	1					
74	Chloroprene latex + CVP	5	5					
75	10 HCBD - 90 Ip	5	4	4	.45	.40	.43	.53
76	20 HCBD - 80 Ip	5	4	2	.82	.88	.85	1.04
77	10 PAAP - 90 Ip	5	4	1				
78	20 PAAP - 80 Ip	5	2	1				

Terpolymers of butyl acrylate (BA) vinylidene chloride (VCl_2) and diallyl chloromethylphosphonate were prepared and found to be self-extinguishing. Even copolymers of BA and VCl_2 were self-extinguishing. In the presence of DACP, the low temperature flexibility was improved. Table III summarizes compositions which have been prepared and the flame retardance obtained. The self-extinguishing property of materials prepared in the presence of DACP is characterized by the formation of a protective film upon exposure to the flame.

The charge compositions of these preparations were selected with the aid of triangular graph paper to facilitate subsequent correlation of properties vs. composition as discussed by Grinsfelder, "Design of Experiments", Resin Review, No. 14, March 1955 (available from Rohm & Haas Co., Resinous Products Division. Philadelphia, Pa.).

Thus, at a ratio of BA to DACP of one to one, samples 75-37-85, 93, 92 are a group of increasing VCl_2 charge compositions while at a BA to DACP ratio of approximately 4 to 1, samples 75-37-84, 81, 82 represent another group of increasing VCl_2 charge compositions. All compositions in Table III except #75-37-87 may be fitted into this scheme. For convenience, Table IV groups the related compositions. In each group, a plot of a measured property of the sample indicated against the % of varying monomer, shows the effect of changes in the content of the varying monomer at a fixed ratio of the other two components. It should be re-emphasized, however, that the compositions refer to monomer charge compositions and not necessarily the final polymer compositions.

Table III

Summary of Preparation of "Flame Retardant" BA-VCl_2 DACP Polymers

Experiment No. PRL-	Sample No. 75-37-	Composition(Wt. %)				% Conversion	Flame Retardance QM#
		BA	VCl_2	DACP	AN		
172-148-1	93	33.3	33.3	33.3	--	78	4
-2	81	66	17	17	--	78	4
-3	92	17	66	17	--	85	4
-4	91	17	17	66	--	77	4
172-150-1	82	45	45	10	--	85	4
-2	83	75	20	5	--	92	4
-3	84	75	5	20	--	88	4
-4	85	45	10	45	--	76	4
204-6-1	90	50	50	--	--	97	4
-2	88	80	20	--	--	98	4
204-8-1	86	62	27	11	--	82	4
-2	87	62	17	11	10	45	4
200-24-3	89	65	28	7	--	87	4

Table IV

Percent of Varying Monomer at Fixed Ratios
of Two Other Monomers of Three Monomer Compositions

Fixed Monomers	Fixed ratio of these Monomers	Varying Monomer	Sample No. 75-37-	% of varying Monomer
BA/DACP	1/1	VCl_2	85	10
			93	33.3
			92	66
BA/DACP	4/1	VCl_2	84	5
			81	17
			82	45
BA/VCl	4/1	DACP	88	0
			83	5
			81	17
			85	45
BA/VCl_2	7/3	DACP	89	7
			86	11
BA/VCl_2	1/1	DACP	90	0
			82	10
			93	33
			91	66
VCl_2/DACP	4/1	BA	83	75
			89	65
			82	45
			92	17
VCl_2/DACP	1/1	BA	81	66
			93	33.3
VCl_2/DACP	1/4	BA	83	75
			85	45
			91	17

Other self-extinguishing elastomers have been prepared by the incorporation of a CVP-prepolymer ("CVP-syrup") in conventional elastomers such as Acrylon BA-12.

Although CVP does not ordinarily homopolymerize, it was discovered that by use of a high temperature initiator such as tert. butylhydroperoxide at about 130°C, a syrupy, low molecular weight polymer was formed. This CVP-syrup could be cured to a hard, non-burning resin with zinc oxide or magnesium oxide along with dicumyl peroxide at 200°C. On the rubber mill, CVP-syrup containing zinc oxide and dicup was milled into elastomers and then cured at 200°C for 30 minutes.

CVP-syrup was milled into Neoprene W polymer as well as into a copolymer of 50% of butyl acrylate and 50% of vinylidene chloride. The flame retardance of the resulting product was only slightly better than the uncompounded elastomer. Both products were still rated as self-extinguishing (QM#4). Both products were too soft to be of practical value.

Soft semi-solids were also obtained when CVP-syrup was combined with Acrylon EA-5, low molecular weight copolymers of ethyl or butyl acrylate and acrylonitrile, or acrylate monomers under curing conditions.

One of the most promising flame-retardant monomers was diallyl allylphosphonate. Unlike most of the other phosphonates, it homopolymerizes readily to give highly cross-linked, non-flammable resin (QM#5). However, terpolymers with BA and VCl_2 as well as the 50-50 copolymer with BA burned readily. Table V summarizes the compositions investigated:

Table V

Summary of Preparation of BA - VCl_2 - DAAP Polymers

Expt. No. PRL-204-12	Composition (Wt.%) BA	VCl_2	DAAP	% Conversion	Flame Retardance QM#
1	50	---	50	86	1-2
2	66	17	17	87	2
3	75	20	5	93	3
4	75	5	20	93	1

Since neoprene was a self-extinguishing polymer, its monomer, chloroprene, was considered as a flame-retardant monomer for copolymerization. However, when more than 10% by weight of total composition was isoprene, a flammable polymer was obtained.

EXPERIMENTAL

1. Emulsion Polymerization of Isoprene in Presence of CVP

A typical copolymerization recipe for the emulsion polymerization of isoprene with CVP consisted of:

Total monomers:	100 parts by weight
Water	185
Sodium sulfoxylate formaldehyde	0.75
Diisopropylbenzene hydroperoxide	0.30
Proprietary surfactant	20.0

The monomer mixture consisted of up to 25% CVP, the next being isoprene purified by percolation through an alumina column.

All components were combined and heated to 35-40°C on a water bath with stirring for the first 6 hours and then finished at room temperature for 18 hours. The crud was separated and the latex coagulated with isopropanol. The coagulum was dried in a vacuum oven for 24 hours at room temperature. Upon aging, polymers prepared with CVP were found to become flammable.

2. Terpolymerization with CVP and Acrylonitrile

A series of terpolymers of iosprene, CVP, and acrylontrile in various proportions was prepared with the object of finding a composition which would exhibit flame-retardance as well as solvent resistance. The flame retardance of freshly purified and dried terpolymers varied from QM#1 to QM#5. The physical appearance of these polymers ranged from soft, tacky elastomers, through tough rubbers, to powders.

A monomer composition containing only 15% isoprene gave a rubbery polymer, whereas, in the absence of isoprene, a powder was obtained.

A high concentration of CVP (40%) did not appreciably retard a reaction in which 30% AN was present.

Table VI shows the compositions, yields and initial flame retardance of these polymers. Upon aging, all of these polymers too became flammable.

Table VI

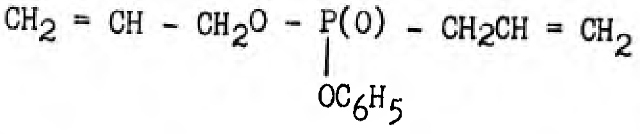
Charge Composition and Flame Retardance
AN-CVP-Ip Emulsion
Copolymerization

Experiment	Shipping No. 75-37	Initial Charge % Compositions			% Yield	Initial Flame Retardance
		A.N.	C.V.P.	I.p.		
164-24A	68	4.5	4.5	91	52	4
-24B		9.0	9.0	82	57.5	1
-24C		16.5	16.5	67	60.0	2
-24D	69	8.0	4.5	87.5	47.5	4
-24E	70	15.0	8.5	76.5	76.2	4
-24F	71	27.0	14.8	58.2	72.0	5
164-25A		16.0	4.0	80.0	73.0	1
-25B		28.0	7.0	65.0	73.0	1
-25C		30.0	3.3	67.0	61.0	1
164-27A		44.3	11.0	44.5	74.7	1
-27B		7.0	19.0	74.0	77.0	4
-27C		40.0	20.0	40.0	62.5	3
164-28A		65.0	35.0	0.0	62.0	5
-28B	72	55.0	30.0	15.0	10.0	4
-28C	73	30.0	40.0	30.0	50.0	4

3. Copolymerization of Isoprene with Other Monomers

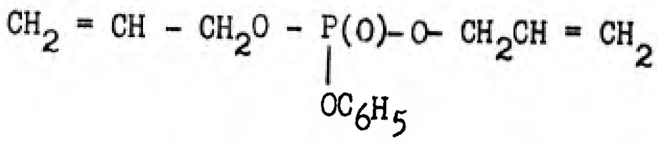
Allyl phenyl allylphosphonate: By emulsion techniques monomer charges containing 10 and 20% respectively of allyl phenyl allylphosphonate, the rest being isoprene, were polymerized slightly above room temperature for 24 hours. Yields were 35 and 48% respectively. The initial flame retardance of the polymers were QM#5. Polymers prepared with 30 and 40% allyl phenyl allylphosphonate were prepared in 73 and 65% yields. Both polymers burned. After a short storage period the earlier polymers also burned.

Diallyl Phenyl Phosphate: A compound, closely related to allyl phenyl allylphosphonate (I),diallyl phenyl phosphate (II) was also polymerized at the 10 and 20% level in isoprene. Yields were 56 and 52% respectively after 24 hours. The initial flame retardances of the polymers were QM#5. However, on aging, this elastomer lost flame retardance.



$CH_2 = CH - CH_2O - \underset{OC_6H_5}{\underset{|}{P(O)}} - CH_2CH = CH_2$

(I)



$CH_2 = CH - CH_2O - \underset{OC_6H_5}{\underset{|}{P(O)}}-O- CH_2CH = CH_2$

(II)

Hexachlorobutadiene: Solutions of isoprene with 5, 10, and 20% hexachlorobutadiene (HCBD) were polymerized in emulsions. The flame retardance of the polymer isolated from the 5% HCBD-95% isoprene system initially was QM#4, the other polymers initially had a QM#5. Polymers were also prepared with charges of 30, 40, 50, 56.1,and 79.3% of hexachlorobutadiene. After repeated purification and drying, all of these polymers burned.

Copolymerizations of Butyl Acrylate - Diallyl Chloromethylphosphate Systems

The polymerizations of BA-DACP with and without vinylidene chloride and acrylonitrile were carried out with a water to monomer ratio of 5 to 3, 5% emulsion polymerization grade of sodium laurylsulfate (e.g. Dupanol WAQE), 0.34% hydrogen peroxide (100% active), and 0.51% sodium sulfoxylate formaldehyde on the monomer. The polymerization was activated with one drop of a 0.2% solution of ferrous ammonium sulfate (1260) or one drop of a ferric thiocyanate solution (0.06% solid).

Typical monomer compositions are given in Table III.

Preparation of CVP-Syrup

In a 2 l.-3 necked flask fitted with stirrer, reflux condenser, addition funnel, thermometer, and nitrogen inlet, was placed 200 g. of CVP monomer. Under a steady flow of nitrogen, and with stirring, the temperature of the monomer was raised to 135°C. Then 1 ml. of tert.-butyl hydroperoxide was added and the temperature was maintained so as not to exceed 140°C. When the exothermic phase of the reaction is over, another ml. of tert.-butyl hydroperoxide is added with the same precautions as before. This procedure is repeated until 9.2 g. (appr. 10 ml.) of tert.-butyl hydroperoxide has been added (about 1.5 hours). Then the temperature is raised to 140°C for 10 minutes (Note 1.)

Then a solution of 37 g. of tert.-butyl hydroperoxide in 800 g. of CVP is added at such rate that the temperature of the flask content is maintained at 138°C. ± 1°. Some regulation of the heat input may be required. The addition requires about 4.5 hours. The temperature is then raised to 150°C. and maintained at that temperature for one hour. The syrupy product is most conveniently removed from the flask while still warm.

Note 1: The temperature control in the initial phases of the preparation is critical. In several cases where the reacting temperature was allowed to rise above approximately 150° in the early stages, a vigorous exotherm was observed with product foaming out of the flask. In cases where this happened, a low boiling by-product was formed in substantial amounts. This has been identified as 1,2-dichlorethane. In one case, the residual polymer from a run-away reaction was a hard, infusible, foamed material.

Utilization of CVP - Syrup

Syrups prepared by the above method were milled into Acrylon BA-12 and Acrylon EA-5 along with "dicup" and magnesium or zinc oxide. The Acrylon EA-5 containing material, after curing, was a viscous tar-like material which would require further vulcanization to give rubbery products. The Acrylon BA-12 containing material was less fluid when 50% CVP Syrup had been incorporated.

Other work with CVP-Syrup was carried out by mixing liquid Acrylon compositions or butyl acrylate monomers with peroxide catalysts. Upon heat-curing somewhat fluid tar-like materials resulted.

A typical procedure for the incorporation of CVP-syrup in an Acrylon rubber is the following:

A solution of 200g of CVP syrup and 4g. of dicumyl peroxide was prepared in a tared container (Solution A).

On a cold rubber mill, 400g. of Acrylon BA-12 was broken down and 4g. of stearic acid added. Gradually 150 grams of solution A was milled into the rubber. After this material had been well dispersed, 1.5g of zinc oxide was milled in. The product was stripped off the rolls and cured for 30 minutes at 200°C. (Approximately 26% CVP in the composition).

The product was returned to the mill and an additional 65g. of Solution A was milled in. The material was sheeted and cured at 200°C for 30 minutes. The product contained 35% CVP.

By a similar procedure CVP-syrup was incorporated in Neoprene W and the 50-50 BA-VCl_2 copolymer.

Samples Submitted to The Contractor:

Table VII lists the samples submitted to the Quartermaster Research and Development Command during the second contract year. Of the samples 75-37-65 up to and including 75-38-78, only 75-37-74 had permanent self-extinguishing characteristics. The remaining samples were all self-extinguishing.

Table VII

List of Samples Submitted to the Quartermaster Research and Development Command

	Monomer Charge Composition by weight							
Sample No. PRL	% CVP	% Ip	AN	HCBD	PAAP	BA	VCl_2	DACP
75-37-65	15	85						
66	15	85						
67	15	85						
68	4.5	91	4.5					
69	4.5	87.5	8.0					
70	8.5	76.5	15.0					
71	14.8	58.2	27					
72	30	15	55					
73	40	30	30					
74	Chloroprene later treated with CVP							
75-38-75		90		10				
76		80		20				
77		90			10			
78		80			20			
79	Cured sample of Acrylon BA-12 with 35% CVP-Syrup							
80	Sample of CVP-Syrup PRL 200-18							
81						66	17	17
82						45	45	10
83						75	20	5
84						75	5	20
85						45	10	45
86						62	27	11
87			10			62	17	11
88						80	20	--
89						65	28	7
90						50	50	--
91						17	17	66
92						17	66	17
93						33.3	33.3	33.3