

**RESEARCH ON HEAT-RESISTANT ACRYLATE-SILOXANE
ELASTOMERS**

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FOREWORD

This report was prepared by Bjorksten Research Laboratories, Inc., to describe the work performed under USAF Contract No. 33(616)-2135 during the period 8 June 1953 - 15 August 1954. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials," Task No. 73404, "Synthesis and Evaluation of New Polymers," formerly RDO No. 617-11, "Synthesis and Evaluation of New Polymers," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with 1st Lt. E. C. Stump acting as project engineer.

The work was performed at Bjorksten Research Laboratories, Madison, Wisconsin, with Mr. R. P. Cox as initial project leader, later succeeded by Mr. L. L. Yaeger. Contributing staff members were Mr. R. W. Buetow, Mr. K. Guenther, Dr. H. Hamilton, and Miss M. Bubolz. The report was edited by Miss B. A. Harker.

We are grateful to Dr. M. Jellinek and associates, Linde Air Products Tonawanda Laboratory, for the preparation of specialized siloxanes; and to Dr. A. M. Borders, Minnesota Mining & Manufacturing Company, and the American Monomer Corporation for information on the compounding of elastomers and for samples of commercial acrylic elastomers.

ABSTRACT

The objective of this project was the synthesis of acrylate-siloxane elastomers with good thermal and solvent resistance. Of the many polymers investigated as gum rubber bases, vinyl triethoxysilane-acrylonitrile-ethyl acrylate compositions were the best as measured by (1) swelling in 70-30 iso-octane-toluene and in Penola oil and (2) weight loss and flexibility after heating in air at 350°F.

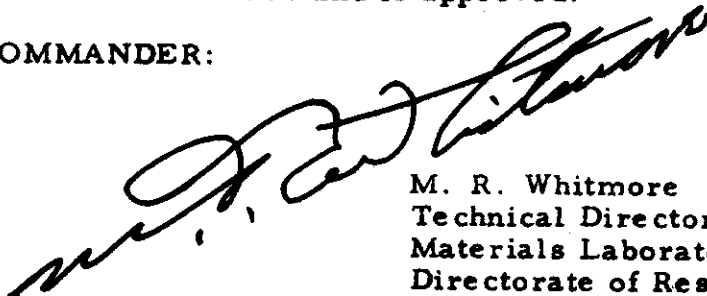
The addition of either dibutyl phosphite or polychlorotrifluoro ethylene powder (Kel F) to these gum rubbers generally maintained their flexibility in air at 350°F. for 250 to 1000 hours. As a reinforcing filler to provide good tensile strength, carbon black (Philblack O) was superior to other fillers tested. Trimene Base was effective as a vulcanization accelerator throughout this work.

The vinyl triethoxysilane-ethyl acrylate gum rubbers could be vulcanized without additives through the formation of cross-linkages. Cross-linking probably took place through adjacent >SiOH groups formed in emulsion polymerization.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. Whitmore
Technical Director
Materials Laboratory
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INTRODUCTION

Under Contract AF 33(600)-23723, various materials were investigated for use as heat-resistant interlayer materials for laminated glass and laminated plastic. The optimum interlayer material was a copolymer of ethyl acrylate and vinyl polysiloxane. This work is described fully in WADC Technical Report 54-57.

The project described in this report was initiated as an outgrowth of the work performed under the above contract. The objective of this project was the synthesis of acrylate-siloxane elastomers with the following characteristics:

- (a) Retention of rubberlike properties in the temperature range -65°F. to 400°F. , and
- (b) Resistance to petroleum oils, fuels, diesters, alkyl phosphates, and silicone oils.

In the preparation of gum rubber compositions, primary consideration was given to the following variations in composition:

- (a) Acrylate and methacrylate monomers selected from those commercially available.
- (b) Silane and siloxane monomers or polymers selected from those commercially available.
- (c) Additives, stabilizers, modifiers, and fillers selected from commercially available materials known to improve the properties of gum rubber compositions.

Initial polymerization runs were made with ethyl acrylate to determine the optimum emulsion polymerization technique and recipe. This work is described in Section I.

Procedures used to prepare and test gum rubbers are given in Section II. The results of screening tests and the effects of various antioxidants, stabilizers, modifiers, and fillers on the properties of gum rubbers are discussed in Section III.

On the basis of the screening tests, gum rubbers containing ethyl acrylate and vinyl triethoxysilane were selected as the most promising from the standpoint of thermal and solvent resistance. Attention was therefore centered on these compositions in the final stages of the project (Section IV).

Two experimental designs were carried out on the use of additives for maintaining the flexibility of vulcanizates of vinyl triethoxysilane-ethyl acrylate gum rubbers when exposed to high temperatures. Low-temperature tests and long-range aging tests were performed on these vulcanizates. A short

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theoretical investigation was also conducted on the cross-linking mechanism of vinyl alkoxysilanes.

Conclusions and recommendations for further work in this field are given in Section V.

A bibliography on acrylate and related elastomers is included at the end of the report.

I. EMULSION POLYMERIZATION TECHNIQUES

Initial polymerization runs were made with ethyl acrylate to determine the following:

- (a) Optimum emulsifying agent.
- (b) Effect of catalyst concentration on the rate of polymerization.
- (c) Effects of modifier concentration on the rate of polymerization and the molecular weight of the polymer.
- (d) Effect of time on emulsion polymerization.

A. Emulsifying Agents

The stock formulation and emulsifiers used in the initial polymerization runs were:

<u>Stock Formulation</u>	<u>Amount (grams)</u>
Water	70.0
Cumene hydroperoxide	0.085
Sharples 3B mercaptan	0.25
Fructose	0.25 (As 10 milliliters of 2.5% solution)
FeSO ₄	0.0035 (As 20 milliliters of stock solution)
Na ₄ P ₂ O ₇ · 10H ₂ O	0.75
Ethyl acrylate	50.0

<u>Emulsifier</u>	<u>Amount (grams)</u>
Petronate	2.25
Petronate H	2.25
Ultrawet K	1.25
Ultrawet 60L	1.25
Aerosol OT	1.50
Santomerse TIB	1.50
Santomerse B	1.50

The water and emulsifying agents were placed in an 8-ounce bottle fitted with a plastic screw cap and a self sealing rubber liner protected with an aluminum insert. The bottle was then sealed, placed in the 40°C. emulsion polymerization water bath (Figure 1), and revolved at 28 rpm until the emulsifier dissolved (30 minutes).

After the addition of the cumene hydroperoxide, fructose, and iron activator (in that order), a mixture of ethyl acrylate and mercaptan was added. The bottle was then swept with nitrogen, capped, and placed in the emulsion polymerization bath.

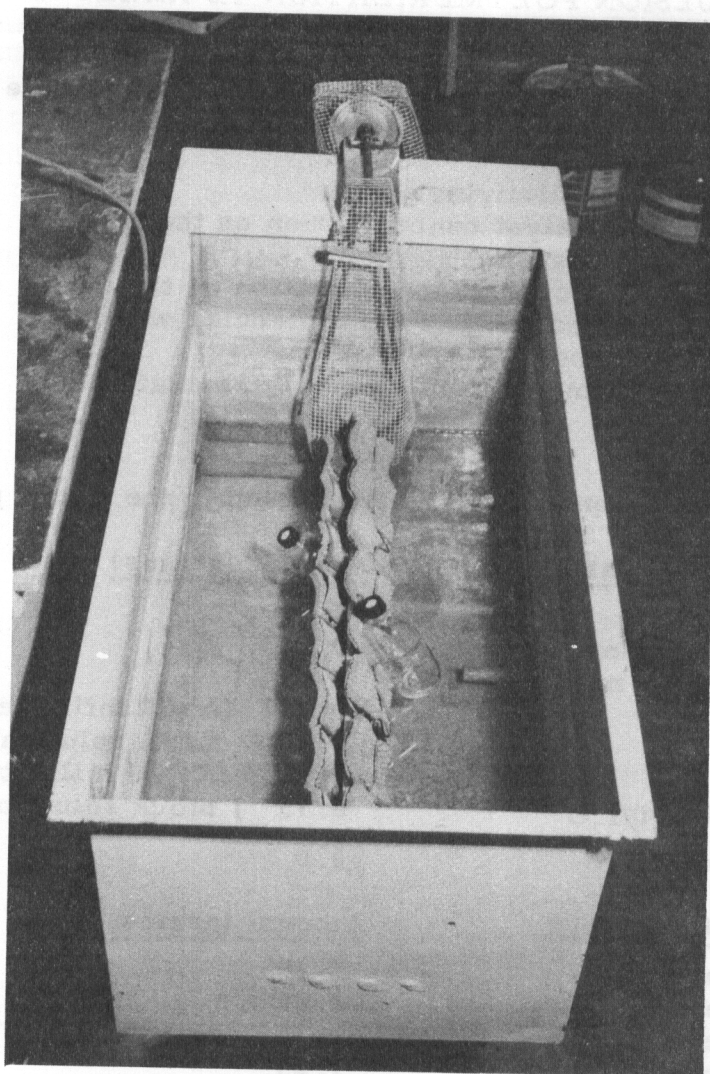


Figure 1. Emulsion Polymerization Bath.

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Conversion data were obtained by taking 4-milliliter samples, by means of a hypodermic syringe, at prescribed intervals, placing these samples in previously weighed aluminum weighing pans containing a few crystals of hydroquinone, and drying at 80°C. The effects of the different emulsifiers on the percent of conversion are shown in Figure 2. Santomerse B gave the fastest rate of conversion as well as the highest percent of conversion.

B. Effect of Catalyst and Modifier Concentration

The stock formulation in these experiments consisted of 50 grams of ethyl acrylate and 90 milliliters of a 1.6% solution of Santomerse B in distilled water, rather than the complicated recipe used in the work on emulsifying agents.

The effect of catalyst concentration on the rate of polymerization was determined by maintaining a constant mercaptan level of 50 drops and varying the amount of ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, in three samples, i. e., by the addition of 2, 4, and 8 milliliters of a 3.12% solution in distilled water.

Figure 3 illustrates very clearly the marked rate determining effect of the catalyst concentration; curves 1, 2, and 3 represent increasingly higher concentrations.

The effect of the modifier (Sharples 3B mercaptan, tertiary dodecyl) on polymerization rate was determined similarly. The modifier concentration was varied by the addition of 0, 2, 4, 6, 8, 10, 20, and 40 drops to stock samples containing 10 milliliters of 3.12% ammonium persulfate (which was judged from the previous experiment to be sufficient catalyst to provide a maximum rate).

A plot of the conversion data (Figure 4) reveals that, although a lag period appears with lower concentrations, the conversion is essentially complete at the end of two hours regardless of concentration. As a consequence, the effect of modifier concentration as a rate determining factor may be ignored.

On the other hand, Figure 5, in which the modifier concentration is plotted against the relative molecular weight of the polymer (flow time through an Ostwald Viscometer of 1% solutions of polymer in dioxane at 35°C.) emphasizes the marked effect of the modifier on the molecular weight.

Propylene glycol monomethacrylate (PGMM) was synthesized (see Appendix A) and copolymerized with ethyl acrylate. Data on the rate of copolymerization (Figure 6) reveal that the inhibitory effect of PGMM is partly overcome by the mercaptan. However, this effect reaches a maximum at 10% PGMM and higher concentrations result in no further inhibition.

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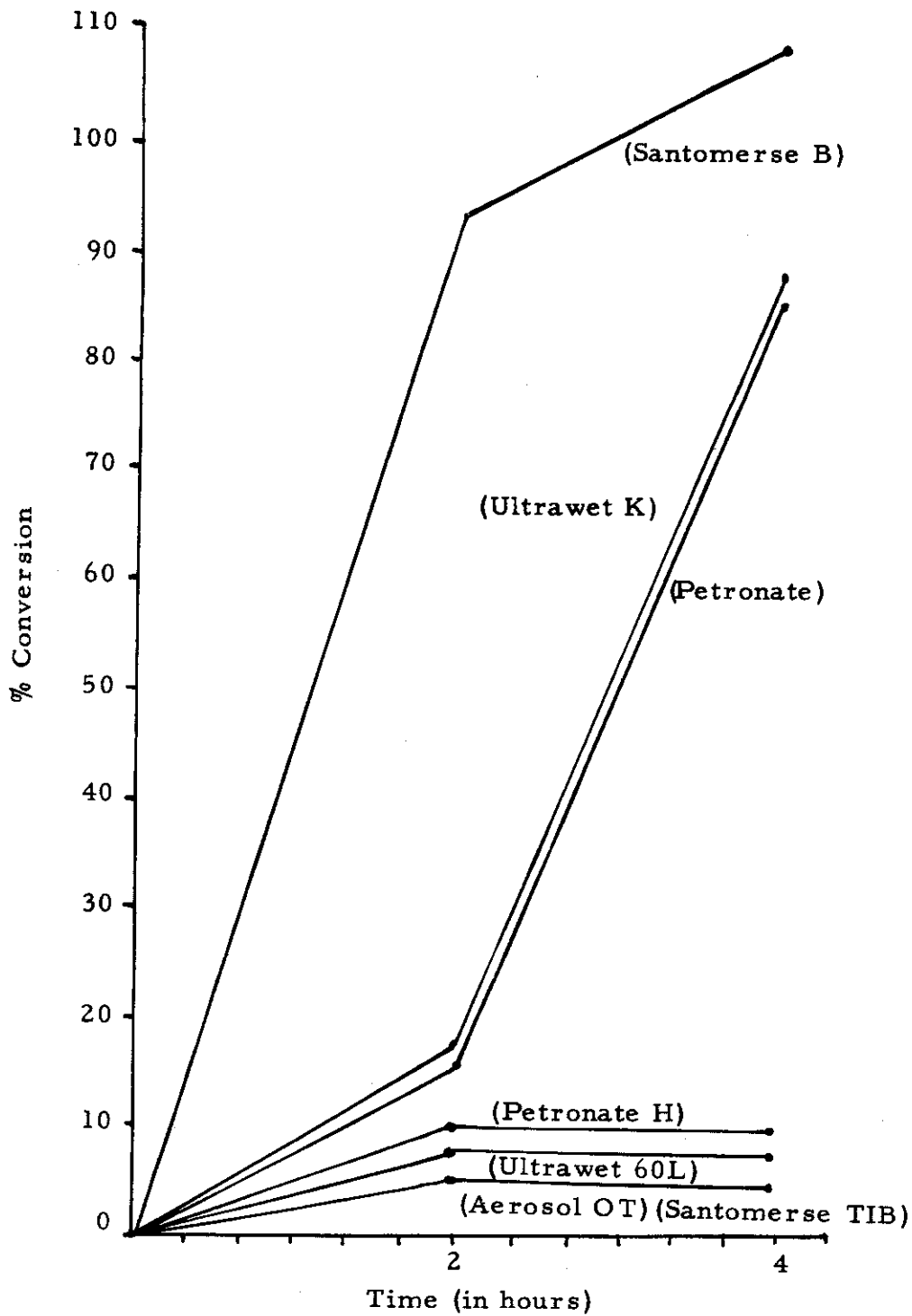


Figure 2. Effect of Emulsifier on Rate of Polymerization of Ethyl Acrylate.

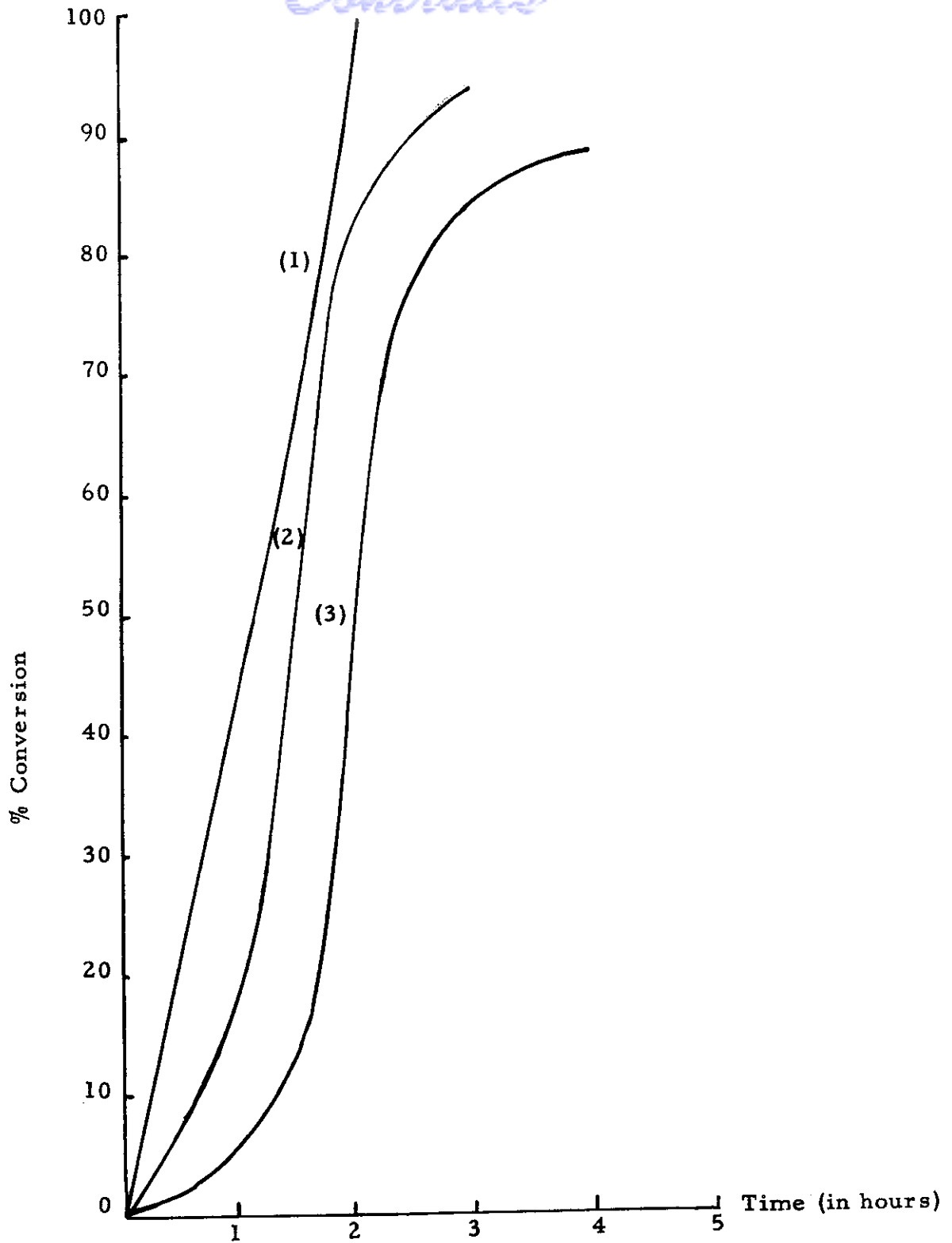


Figure 3. Effect of Ammonium Persulfate Concentration on Rate of Polymerization of Ethyl Acrylate.

- (1) 2.0 ml. of 3.12% solution.
- (2) 4.0 ml. of 3.12% solution.
- (3) 8.0 ml. of 3.12% solution.

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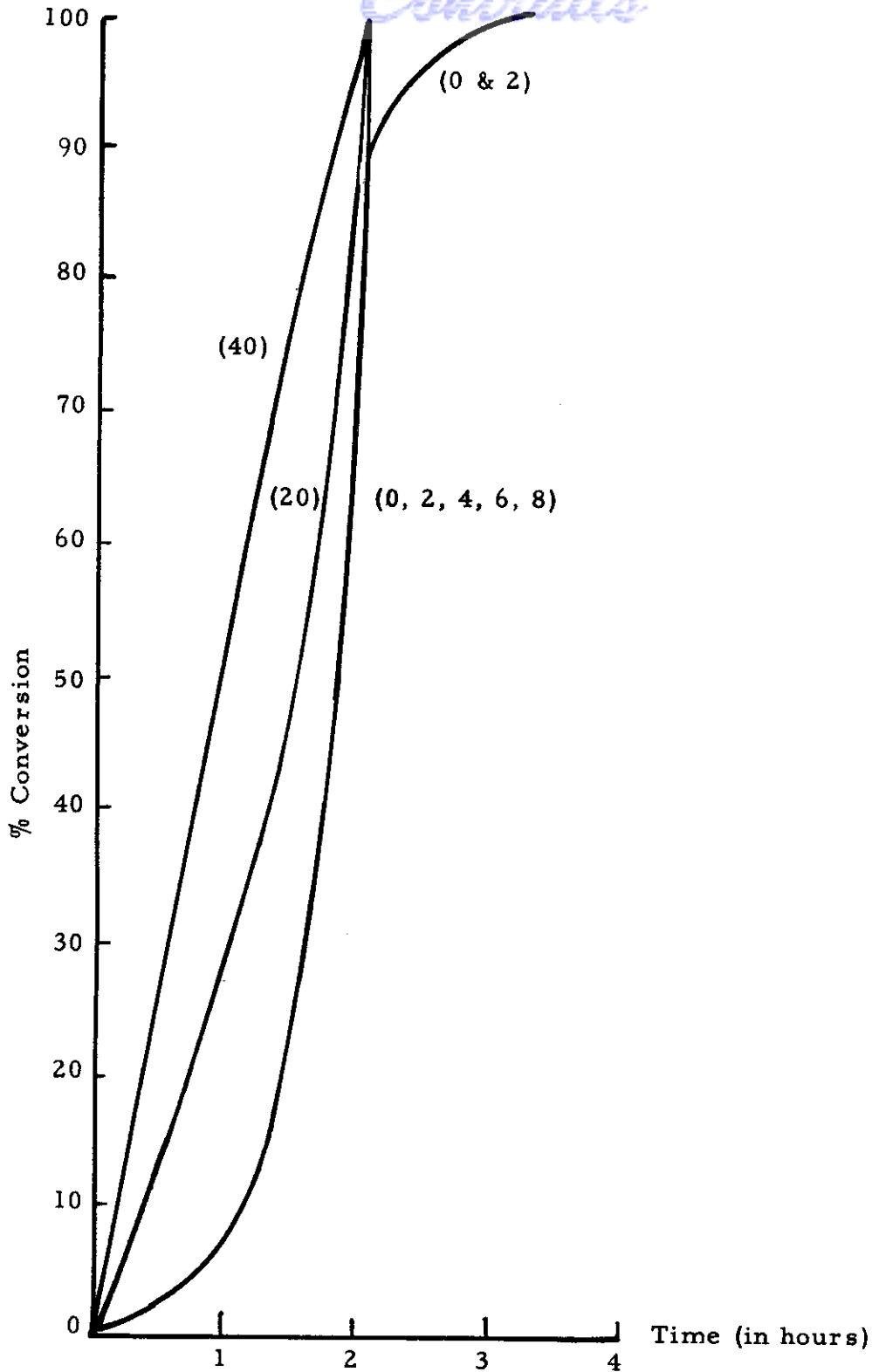


Figure 4. Effect of Modifier Concentration on Rate of Polymerization of Ethyl Acrylate. (Numbers in parentheses indicate the number of drops of modifier which were added.)

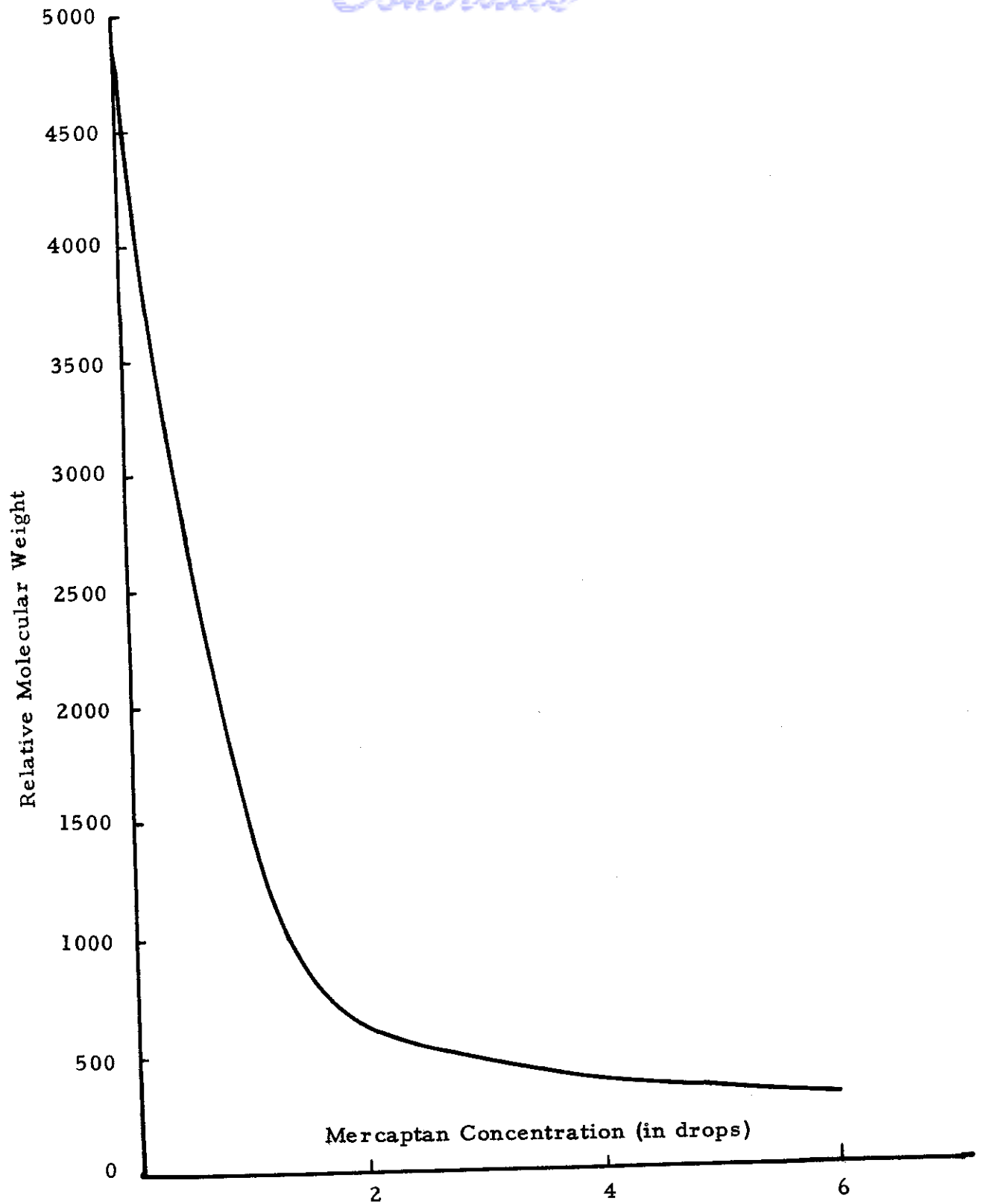


Figure 5. Effect of Modifier Concentration on Relative Molecular Weight of Polymer.

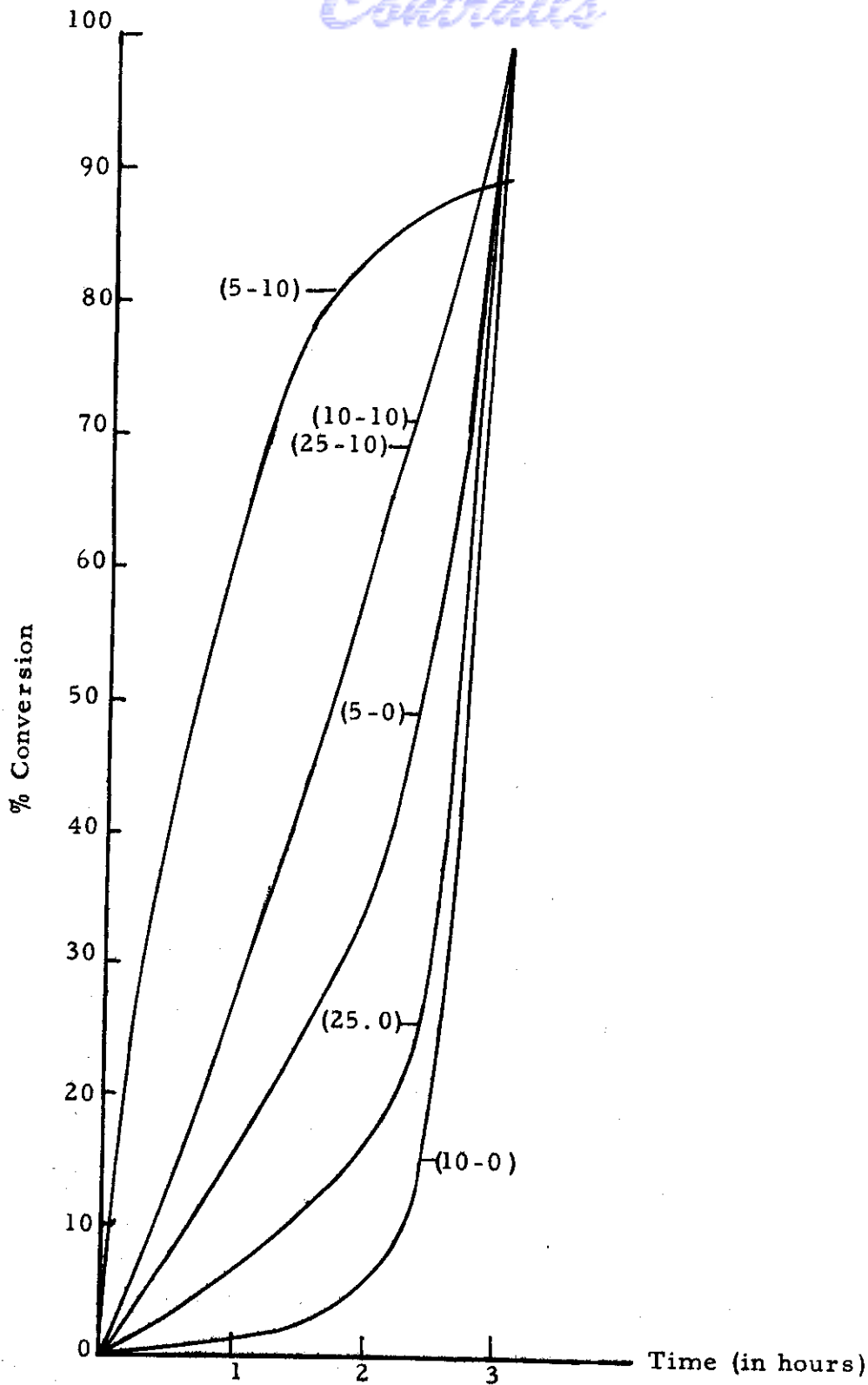


Figure 6. Effect of Modifier Concentration on Rate of Copolymerization of Ethyl Acrylate and Propylene Glycol Monomethacrylate. (Numbers in parentheses indicate PGMM concentration and drops mercaptan, e.g., (25-10)=25% PGMM and 10 drops mercaptan.)

Conclusions

This work demonstrates that the generalization arrived at from Figure 4 for polymerization of pure ethyl acrylate is also valid for copolymerization, i. e., although omission of the mercaptan results in a slower initial rate, it does not affect the time necessary to obtain complete conversion, which in this case is three hours. From the preceding data it is apparent that as long as an excess of catalyst is used the overall polymerization rate is independent of mercaptan concentration. In addition, the molecular weight of the polymer is inversely proportional to the mercaptan concentration. Hence, a very useful means is available for controlling the molecular weight of the polymers without affecting their rate of formation.

C. Effect of Time

To determine the effect of time on the percent of conversion in emulsion polymerization, identical samples were agitated for 2, 6, and 24 hours at 50°C. The composition of the reaction mixture was:

Ethyl acrylate	45 grams
Beta chloroallyl alcohol	5 grams
1.67% aqueous solution of Santomerse B	90 milliliters
Sharples 3B mercaptan	0.5 gram
3% aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$	10 milliliters

The times for efflux (Ostwald Viscometer) of 1% dioxane solutions of these products at 35°C. were as follows:

Sample No.	Period of Polymerization (hours)	Time of Efflux (seconds)
VE-107-3	2	266
VE-107-5	6	276
VE-107-6	24	276

Thus, the samples may safely be agitated for periods exceeding the time necessary for 100% conversion.

II. PROCEDURES FOR PREPARING AND TESTING GUM RUBBERS

A. Preparation of Gum Rubbers and Vulcanizates

Based on the work described in Section I, we selected the following stock formulation for the preparation of gum rubbers by emulsion polymerization:

Monomer	50 grams
1.67% aqueous solution of Santomerse B	90 milliliters
3% aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$	10 milliliters
Sharples 3B mercaptan	0-20 drops (depending on the molecular weight desired)

The mercaptan and monomer (or monomers) were mixed well and added to the aqueous solution of catalyst and emulsifying agent. The bottles containing the polymerization mixture were flushed out with carbon dioxide or nitrogen gas, capped, and tumbled in the emulsion polymerization bath (Figure 1) at 50°-52°C. The emulsion was steam distilled for 1/2 hour and coagulated by addition of solid NaCl. The coagulum was pressed into a band on a modified washing machine wringer, washed, and partly dried on a Thropp mill. The temperature of the oil circulating through the hot roll of the mill was kept at 260°-300°F. The drying was completed by heating for two days at approximately 50°C. in a vacuum oven.

In the preparation of vulcanizates, the gum rubbers were compounded with fillers and other additives on the Thropp mill (oil temperature of 260°-300°F.). After 2-3 minutes of milling, the sheet was removed from the mill, folded several times, and replaced on the mill. This procedure was repeated three times.

Vulcanization was carried out in either of two circular molds of 0.060-inch depth and 2-inch radius. Cellophane was used as the parting agent. Initially the vulcanization cycle was 1-3 hours at 155°C.

B. Testing Procedure

The testing procedure used in evaluating all samples was as follows:

After vulcanization (standardized as one hour at 155°C.) samples which contained bubbles or were weak were rejected. Before final rejection, such compositions were usually dried and vulcanized for three hours at 155°C. in an attempt to prepare a strong and bubble-free sample. All compositions which passed the above crude tests were cut into 15-1/4 inch by 1-1/2 inch strips. Three strips were used for each of the tests below:

- (a) Original tensile strength and hardness. The former was measured with a Dillon tester and the latter with a Shore hardness tester.
- (b) Properties after exposure to air at 350°F. for 250 hours. The weight (to 0.001 gram), width (to 0.01 inch), and thickness (to 0.001 inch) of the samples were measured before exposure. After heating, the samples were reweighed, bent 180° to observe surface-cracking, and tested for hardness and tensile strength. (The latter was computed on the basis of original dimensions.)
- (c) Properties after immersion in 70-30 iso-octane-toluene at 65°F. for 72 hours and in Penola oil (supplier: Pate Oil Co., Milwaukee, Wis.) at 350°F. for 250 hours. The thickness, width, and length of the samples were measured before immersion and the length was remeasured after immersion. The percentage of linear swelling was calculated on the basis of change in length and the tensile strength on the basis of original dimensions.

III. SCREENING OF GUM RUBBER COMPOSITIONS

The compositions of vulcanizates listed in Table No. 1 illustrate some of the approaches which were tried to obtain elastomers with the desired thermal and solvent resistance. The properties of these vulcanizates are listed in Table No. 2. Data for some of the less promising materials, which had inferior properties, are not presented in these tables.

The following acrylic rubbers* were included in the screening test for comparison:

Hycar PA-21
1, 1-Dihydroperfluorobutyl
acrylate (PFBA)

B. F. Goodrich Co.
Minnesota Mining and
Manufacturing Co.

Some of the commercial products which were investigated for compounding with the gum rubbers are listed below:

Material*	Purpose	Manufacturer or Supplier
Trimene Base	Vulcanization accelerator	Carbide & Carbon Chemicals Co.
Polyac	Vulcanization accelerator	E. I. du Pont de Nemours & Co.
Santocure	Vulcanization accelerator	Monsanto Chemical Co.
Kel F (polytri-fluorochloroethylene)	Additive	M. W. Kellogg Co.
Santomerse B	Additive	Monsanto Chemical Co.
Philblack O (carbon black)	Filler	Phillips Chemical Co.
Hi-Sil (colloidal silica)	Filler	Columbia Chemicals Division, Pittsburgh Plate Glass Co.
Silene L (colloidal silica)	Filler	Columbia Chemicals Division, Pittsburgh Plate Glass Co.

* Many of the materials utilized were not developed or intended by the manufacturer for the conditions to which they have been subjected. Any failure or poor performance of a material is therefore not necessarily indicative of the utility of the material under less stringent conditions or for other applications.

COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition * (Grams)	Vulcanizate Composition (Grams)			
		Phil-black O	Trimene Base	Other Additives	Gum Rubber
X-123	Hycar PA-21	10.4	1.04	Stearic acid (0.52)	40
X-124	Hycar PA-21	10.4	1.04	Stearic acid (0.52) Dibutyl phosphite (0.05)	40
X-125	Hycar PA-21	10.5	1.05	Stearic acid (0.52) Dibutyl phosphite (0.26)	40
X-126	Hycar PA-21	10.5	1.05	Stearic acid (0.526) Dibutyl phosphite (0.526)	40
X-127	Hycar PA-21	10.74	1.07	Stearic acid (0.537) Dibutyl phosphite (1.34)	40
X-128	Hycar PA-21	11.11	1.11	Stearic acid (0.555) Dibutyl phosphite (2.78)	40
X-129	Beta chloroethoxy ethyl acrylate (0.75); propylene glycol monomethacrylate (10); ethyl acrylate (39.25)	17.89	1.78	Stearic acid (0.89) Dibutyl phosphite (0.89)	68
X-130	Beta chloroethoxy ethyl acrylate (0.75); ethyl acrylate (48); propylene glycol monomethacrylate (1.25)	16.84	1.68	Stearic acid (0.842) Dibutyl phosphite (0.842)	64
X-131	Beta chloroethoxy ethyl acrylate (0.75); ethyl acrylate (46.75); propylene glycol monomethacrylate (2.5)	17.37	1.74	Stearic acid (0.868) Dibutyl phosphite (0.868)	68
X-132	Ethyl acrylate (88.5); propylene glycol monomethacrylate (10); beta chloroethoxy ethyl acrylate (1.5)	17.89	1.79	Stearic acid (0.89) Dibutyl phosphite (0.89)	68

* Mercaptan was omitted in the polymerization recipe for all gum rubbers listed in this table.

COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)			
		Phil-black O	Trimene Base	Other Additives	Gum Rubber
X-147	Ethyl acrylate (49.5); vinyl triethoxy silane (0.5)	10.39	1.04	Stearic acid (0.52)	40
X-148	Ethyl acrylate (49.5); vinyl triethoxy silane (0.5)	10.53	1.05	Stearic acid (0.53) Dibutyl phosphite (0.53)	40
X-149	Ethyl acrylate (47); acrylonitrile (2.5); beta chloroethoxy ethyl acrylate (0.5)	10.39	1.04	Stearic acid (0.52)	40
X-150	Ethyl acrylate (47); acrylonitrile (2.5); beta chloroethoxy ethyl acrylate (0.5)	10.39	1.04	Stearic acid (0.53) Dibutyl phosphite (0.53)	40
X-151	Ethyl acrylate (46.75); acrylonitrile (2.5); beta chloroethoxy ethyl acrylate (0.75)	10.39	1.04	Stearic acid (0.53)	40
X-152	Ethyl acrylate (46.75); acrylonitrile (2.5); beta chloroethoxy ethyl acrylate (0.75)	10.39	1.04	Stearic acid (0.53) Dibutyl phosphite (0.53)	40
X-153	Ethyl acrylate (46.5); acrylonitrile (2.5); beta chloroethoxy ethyl acrylate (1.0)	10.39	1.04	Stearic acid (0.53)	40
X-154	Ethyl acrylate (46.5); acrylonitrile (2.5); beta chloroethoxy ethyl acrylate (1.0)	10.39	1.04	Stearic acid (0.53) Dibutyl phosphite (0.53)	40
X-155	Ethyl acrylate (96); propylene glycol monomethacrylate (2.5); beta chloroethoxy ethyl acrylate (1.5)	8.57	0.86	Stearic acid (0.43)	33
X-156	Ethyl acrylate (96); propylene glycol monomethacrylate (2.5); beta chloroethoxy ethyl acrylate (1.5)	8.68	0.87	Stearic acid (0.43) Dibutyl phosphite (0.43)	33
X-157	Ethyl acrylate (93.5); propylene glycol monomethacrylate (5.0); beta chloroethoxy ethyl acrylate (1.5)	8.3	0.83	Stearic acid (0.42)	32

COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)			
		Phil-black O	Trimene Base	Other Additives	Gum Rubber
X-158	Ethyl acrylate (93.5); propylene glycol monomethacrylate (5.0); beta chloroethoxy ethyl acrylate (1.5)	8.42	0.84	Stearic acid (0.42) Dibutyl phosphite (0.42)	32
X-161	Ethyl acrylate (92.5); beta chloro ethyl acrylate (2.5); propylene glycol monomethacrylate (5.0). Product reacted with molar amount of $\text{SiCl}(\text{CH}_3)_3$	10.39	1.04	Stearic acid (0.52)	40
X-162	Ethyl acrylate (92.5); beta chloro ethyl acrylate (2.5); propylene glycol monomethacrylate (5.0). Product reacted with molar amount of $\text{SiCl}_3)_3$	10.39	1.04	Stearic acid (0.52) Dibutyl phosphite (0.52)	40
X-170	1,1-Dihydroperfluorobutyl acrylate (PFBA)	12.6	0.36	Stearic acid (0.36) Sulfur (0.36)	36
X-171	1,1-Dihydroperfluorobutyl acrylate (PFBA)	12.6	0.36	Stearic acid (0.36) Sulfur (0.36) Dibutyl phosphite (0.5)	36
X-178	Hycar PA-21	10.26	---	Stearic acid (0.51) Dibutyl phosphite (0.51)	40
X-179	Hycar PA-21	10.53	---	Stearic acid (0.53) Dibutyl phosphite (1.58)	40
X-181	Beta chloroethoxy ethyl methacrylate (0.25); ethyl acrylate (49.75)	7.27	0.73	Stearic acid (0.36)	28
X-182	Beta chloroethoxy ethyl methacrylate (0.5); ethyl acrylate (49.5)	8.83	0.88	Stearic acid (0.44)	34

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TABLE NO. 1 (Cont'd)

COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)			
		Phil-black O	Trimene Base	Other Additives	Gum Rubber
X-183	Beta chloroethoxy ethyl methacrylate (0.75); ethyl acrylate (49.25)	8.57	0.86	Stearic acid (0.43)	33
X-184	Beta chloroethoxy ethyl methacrylate (1.0); ethyl acrylate (49.0)	10.39	1.04	Stearic acid (0.52)	40
X-185	Beta chloroethoxy ethyl acrylate (0.75); propylene glycol monomethacrylate (5.0); ethyl acrylate (44.25)	8.83	0.88	Stearic acid (0.44)	34
X-186	Beta chloroethoxy ethyl acrylate (0.75); propylene glycol monomethacrylate (5.0); ethyl acrylate (44.25)	8.83	0.88	Stearic acid (0.44) Dibutyl phosphite (0.44)	34
X-187	Beta chloroethoxy ethyl acrylate (0.75); propylene glycol monomethacrylate (10); ethyl acrylate (39.25)	8.57	0.86	Stearic acid (0.43)	33
X-188	Beta chloroethoxy ethyl acrylate (0.75); propylene glycol monomethacrylate (10); ethyl acrylate (39.25)	8.57	0.86	Stearic acid (0.43) Dibutyl phosphite (0.43)	33
X-189	Beta chloroethoxy ethyl methacrylate (1.25); ethyl acrylate (48.75)	10.13	1.01	Stearic acid (0.51)	39

TABLE NO. 2

PROPERTIES OF VULCANIZATES

Sample No.	Original Tensile Strength (psi) and Shore Hardness (A)	250 Hr. Exposure to Air at 350°F			72 Hr. Immersion in 70-30 Iso-octane-Toluene at 65°F		250 Hr. Immersion in Penola Oil at 350°F			
		% Wt. Loss	180° Bend	Tensile Strength (psi)	Shore Hardness (A)	% Linear Swelling	Tensile Strength and Shore Hardness (A)	% Linear Swelling	180° Bend	Tensile Strength (psi)
X-123-I	910-65	12.5	F*	-	100	11.5	375-55	7.0	O.K.	290
X-123-II	700-65	14.0	F	-	100	10.5	160-60	6.5	O.K.	290
X-124-I	770-65	12.5	F	-	100	10.5	230-50	9.0	O.K.	320
X-124-II	720-65	6.5	S.C.**	950	100	11.5	245-55	9.5	O.K.	220
X-125-I	700-60	10.0	O.K.	1100	100	13.0	370-45	7.5	O.K.	340
X-125-II	820-60	11.0	S.C.	1150	100	11.0	220-50	10.0	O.K.	530
X-126-I	920-55	11.0	O.K.	1180	95	11.5	325-45	10.0	O.K.	510
X-126-II	1220-55	12.5	O.K.	1520	100	11.5	270-50	13.0	O.K.	340
X-127-I	930-50	10.0	S.C.	1000	100	12.0	380-45	12.0	O.K.	515
X-127-II	1000-50	11.5	O.K.	1340	100	13.0	290-45	12.0	O.K.	470
X-128-I	610-40	9.5	S.C.	680	80	11.5	300-20	16.5	O.K.	340
X-128-II	700-40	11.5	O.K.	940	90	12.0	340-25	15.0	O.K.	250
X-129	- - -	9.5	F	-	-	8.5	370- -	-	-	-
X-130	- - -	8.0	O.K.	1350	100	11.5	480- -	-	O.K.	195
X-131	- - -	7.5	F	-	-	10.0	540- -	-	O.K.	295

* F = Fails

** S.C. = Surface Cracks

Notes: (1) All data on immersed or heated samples are the average of three samples.

(2) Samples marked with "II" were vulcanized for three hours at 155°C. All others for one hour.

TABLE NO.2 (Cont'd)
PROPERTIES OF VULCANIZATES

Sample No.	Original Tensile Strength (psi) and Shore Hardness (A)	250 Hr. Exposure to Air at 350°F			72 Hr. Immersion in 70-3C Iso-octane-Toluene at 65°F			250 Hr. Immersion in Penola Oil at 350°F		
		% Wt. Loss	180° Bend	Tensile Strength (psi)	Shore Hardness (A)	% Linear Swelling	Tensile Strength (psi) and Shore Hardness (A)	% Linear Swelling	180° Bend	Tensile Strength (psi)
X-132	- - -	7.5	F	-	-	9.5	560--	-	O.K.	-
X-147	1400--	14.0	S.C.	460	80	8.5	390--	11.0	O.K.	50
X-148	1500--	7.0	O.K.	900	70	8.0	360--	16.5	O.K.	50
X-149	1400--	15.0	F	-	-	7.0	500--	11.0	O.K.	475
X-150	980--	6.0	O.K.	1150	80	5.0	380--	11.0	O.K.	530
X-151	940--	13.0	F	-	-	7.0	340--	14.0	O.K.	510
X-152	1600--	13.0	F	-	-	6.0	560--	11.5	O.K.	360
X-153	1500--	17.0	F	-	-	7.0	460--	9.5	O.K.	380
X-154	1200--	13.5	F	-	-	7.0	450--	12.0	O.K.	370
X-155	1500--	14.5	F	-	-	8.0	560--	16.0	O.K.	110
X-156	1300--	14.0	F	-	-	7.0	520--	15.0	O.K.	270
X-157	1200--	17.0	F	-	-	6.5	390--	17.0	O.K.	140
X-158	1300--	17.0	F	-	-	7.0	560--	14.5	O.K.	110
X-161	1480--	14.5	F	-	-	8.5	549--	9.5	O.K.	92
X-162	1240--	14.5	F	-	-	9.5	468--	10.5	O.K.	253
X-170	310--	11.5	F	-	-	2.0	187--	1.5	O.K.	189
X-171	310--	9.5	F	-	-	5.5	161--	0.5	O.K.	559
X-178	Too weak	-	-	-	-	-	-	-	-	-
X-179	Too weak	-	-	-	-	-	-	-	-	-

TABLE NO. 2 (Cont'd)
PROPERTIES OF VULCANIZATES

Sample No.	250 Hr. Exposure to Air at 350°F			72 Hr. Immersion in 70-30 Iso-octane-Toluene at 65°F		250 Hr. Immersion in Penola Oil at 350°F				
	Original Tensile Strength (psi) and Shore Hardness (A)	% Wt. Loss	180° Bend	Tensile Strength (psi)	Shore Hardness (A)	% Linear Swelling	Tensile Strength (psi)	180° Bend	% Linear Swelling	Tensile Strength (psi)
X-181	1075--	10.5	O.K.	629	--	10.0	425--	O.K.	14.0	403
X-182	948--	8.0	O.K.	831	-	12.5	418--	O.K.	11.5	328
X-183	1456--	11.0	O.K.	500	-	12.5	435--	O.K.	13.0	338
X-184	1527	10.5	O.K.	787	-	12.5	434--	O.K.	12.5	304
X-185	1066--	13.5	B*	"	-	9.5	545--	-	8.0	B
X-186	1046--	11.5	B	-	-	9.5	526--	-	8.5	B
X-187	1149--	11.0	B	-	-	8.0	177--	-	6.5	B
X-188	651--	10.5	B	-	-	6.5	119--	-	6.5	B
X-189	1156	10.5	O.K.	684	-	10.0	431--	O.K.	11.0	335

NOTE: *B =Brittle

A. Terpolymers of Alpha Methyl Beta (Trimethyl Siloxy) Ethyl Methacrylate with Beta Chloroethoxy Ethyl Acrylate and Ethyl Acrylate

Gum rubbers containing ethyl acrylate, beta chloroethoxy ethyl acrylate, and 5, 10, and 20% of alpha methyl beta (trimethyl siloxy) ethyl methacrylate (see Appendix B for preparation) were compounded with 2% of Trimene Base and 20% of Philblack O. With all three concentrations, the vulcanizates became brittle after 250 hours in air at 350°F. After 250 hours in Penola oil at 350°F., the samples were flexible and the tensile strengths for vulcanizates containing 5, 10, and 20% of alpha methyl beta (trimethyl siloxy) ethyl methacrylate were 400, 290, and 110 psi, respectively. There was a slight increase in swelling as the concentration of the methacrylate increased. The tensile strength of the vulcanizates after immersion in alkylate fuel for 72 hours was roughly independent of composition, but the percentage swelling for 5, 10, and 20% concentrations of alpha methyl beta (trimethyl siloxy) ethyl methacrylate was 11, 10, and 7%, respectively.

Several additional series of vulcanizates were prepared from the gum rubber containing 5% of alpha methyl beta (trimethyl siloxy) ethyl methacrylate.

The presence of sulfur had no effect on the properties of these vulcanizates except that the sulfur-free control had a higher initial tensile strength, indicating that it cured faster.

In an attempt to eliminate embrittlement after air-aging, the following antioxidants were evaluated in 1% concentration:

- Phenyl beta naphthylamine
- N, N-di(beta naphthyl p-phenylene) diamine
- p - Isopropoxy diphenylamine
- Dibutyl phosphite.

Of these, only the phosphite was successful. After 250 hours in air at 350°F., the vulcanizate containing phosphite was still flexible and possessed a tensile strength of 1300 psi. After 72 hours in alkylate fuel, its tensile strength was 240 psi.

In an attempt to increase the heat stability of an alpha methyl beta (trimethyl siloxy) ethyl methacrylate vulcanizate, the addition of 10% of Santomerse B was investigated. After 250 hours in air at 350°F., the sample had a lower weight loss and a higher tensile strength than a similar sample without Santomerse B. There was also a slight increase in residual flexibility. Immersion in alkylate fuel did not significantly affect these properties. Immersion in Penola oil, however, resulted in greater swelling and lower tensile strength for the sample containing Santomerse B than for the control.

Continued

Although promising, the terpolymers containing alpha methyl beta (trimethyl siloxy) ethyl methacrylate were relatively difficult to prepare. They were also inferior in properties to vinyl triethoxysilane - ethyl acrylate compositions, and were therefore de-emphasized in favor of the latter.

B. Vinyl Polysiloxane

The products from the compounding of solid X-31 (Linde Air Products vinyl polysiloxane resin) with photopolymerized polyethyl acrylate were very weak and could not be vulcanized with Polyac or Trimene Base.

When X-31 was dissolved in ethyl acrylate before emulsion polymerization, a granular thermoset material precipitated from the emulsion. The residual emulsion solids could not be vulcanized.

Before discontinuance of this approach, several emulsifiers were screened for their stabilizing effect on the emulsion during polymerization to yield a homogeneous product which might be vulcanized. Solutions containing 1% of the following emulsifiers in the aqueous phase were investigated:

- Duonal G
- Rosin Amine D pentachlorophenate
- Triton A-20
- Triton X-45
- Triton X-155
- Triton X-200
- Ultrawet K
- Ultrawet 60L
- Petronate L
- Santomerse B
- Santomerse TIB
- Aerosol OT

With all of these emulsifiers except the last, the emulsion coagulated. A stable emulsion was produced with 1% of Aerosol OT. Lower concentrations, i.e., 0.1, 0.25, and 0.5%, did not prevent coagulation.

Several copolymer batches containing X-31 were prepared with 1% of Aerosol OT, but none of these could be vulcanized with sulfur, Polyac, or Santocure.

A series of modified X-31 resins were prepared at our request by Linde Air Products Co. In these resins, vinyl trichlorosilane was co-condensed with dimethyl dichlorosilane in order to impart lower functionality and increased flexibility. Copolymerization with ethyl acrylate was attempted but was not successful.

Copolymerization of X-32 resin (cyclohexenyl polysiloxane) with ethyl acrylate was also attempted, but the product could not be vulcanized with Polyac.

C. Chloroallyl Alcohol and Chloroalloxy Trimethylsilane Copolymers of

Ethyl Acrylate

Attempts to copolymerize ethyl acrylate with beta chloroallyl alcohol, gamma chloroallyl alcohol, and gamma chloroallyloxy trimethylsilane yielded gum rubbers which were difficult to vulcanize. The vulcanizates had inferior properties.

D. Vinyl Trimethylsilane Terpolymers

Vinyl trimethylsilane was synthesized (see Appendix B) and polymerized with ethyl acrylate and beta chloroethyl acrylate. Since these products offered no improvement over Hycar PA-21, this approach was terminated.

E. Copolymers of Triallyl Cyanurate and Ethyl Acrylate

Ethyl acrylate was copolymerized with 0.5 - 5.0% of triallyl cyanurate and compounded with zinc oxide, sulfur, Polyac, and stearic acid. At triallyl cyanurate concentrations of over 0.5%, the gums were cheesy and the vulcanizates were weak. At 0.5%, the vulcanizate swelled 24.5% (linear) and had a tensile strength of 140 psi after 250 hours in Penola oil at 350°F. After 250 hours in air at 350°F, it showed surface cracking but had a tensile strength of 420 psi.

F. Evaluation of Modifiers, Additives, and Fillers

1. Surface Saponification with Sodium Hydroxide

A fundamental problem involved in solvent-resistant rubber is that an elastomer must, by nature, be non-polar and thus will be swollen by non-polar solvents. However, if a surface film of a highly polar material is firmly bonded to a non-polar elastomeric base, the resultant product will be penetrated to a smaller extent by non-polar solvents. We accomplished this with acrylate compositions by surface treatment with hot NaOH solutions. In this way, the ester groups at the surface were saponified, yielding highly polar COONa groups.

The work was done on scraps of different compositions in order to check for qualitative effects. In one sample, the swelling in 70-30 iso-octane-toluene was significantly reduced from 10% to 0%; the control swelled about 11%. Over-treatment of the material yielded a brittle surface which cracked on flexure. The final tensile strength depended on penetration of the solvent (swelling) and crack formation in the surface.

Although this type of surface-treated rubber withstood short periods of immersion in Penola oil, extended immersion caused cracking of the skin layer. This approach was therefore terminated.

2. Effect of Additives

a. Antioxidants in Hycar PA-21

Samples of Hycar PA-21 containing various amounts of dibutyl phosphite were prepared (X-123-128 in Tables 1 and 2). At dibutyl phosphite concentrations of less than 0.1%, the vulcanizate became brittle after 250

hours in air at 350°F. The weight loss (%) did not vary with the phosphite concentration. For Hycar PA-21 samples exposed to air at 350°F. for 500 hours, the critical phosphite concentration was 1%; all vulcanizates with smaller phosphite concentrations became brittle. The linear swelling (%) of samples immersed in alkylate fuel at 65°F. for 72 hours and in Penola oil at 350°F. for 250 hours was independent of the phosphite concentration.

When Hycar PA-21 was milled with up to 3% of dibutyl phosphite but with no Trimene Base, the products were too weak to test (X-178-179 in Tables 1 and 2). The dibutyl phosphite is therefore not a stable cross-linking agent.

In addition to dibutyl phosphite, a series of other commercial antioxidants were screened for use in stabilizing Hycar PA-21 against embrittlement when heated in air. N, N-diphenyl para-phenylenediamine and para-hydroxy diphenylamine were equivalent to dibutyl phosphite in this respect. Phenyl beta-naphthylamine, N, N-di(beta-naphthyl) para-phenylenediamine, aryl alkylated diphenylamine mixture, monobenzyl ether of hydroquinone, and para-isopropoxy diphenylamine were ineffective at 1% concentration.

b. Dibutyl Phosphite in Ethyl Acrylate Polymers

A series of terpolymers of ethyl acrylate, propylene glycol monomethacrylate, and beta chloroethoxy ethyl acrylate was prepared in which the amount of propylene glycol monomethacrylate was varied. The products were compounded with and without 1% of dibutyl phosphite (X-155-158 in Tables 1 and 2). The phosphite did not prevent embrittlement on prolonged heating at 350°F. When the terpolymer was reacted with trimethyl chlorosilane before compounding of the vulcanizate (X-161-162), the phosphite still did not prevent embrittlement.

The compositions and properties of vulcanizates prepared from another series of terpolymers of ethyl acrylate, propylene glycol monomethacrylate, and beta chloroethoxy ethyl acrylate compounded with dibutyl phosphite are also given in Tables 1 and 2 (X-129-132, X-185-188).

Ethyl acrylate was copolymerized with 1% of vinyl triethoxysilane and compounded with and without dibutyl phosphite (X-147-148). The vulcanizates containing phosphite had greatly increased stability in air at 350°F., as compared to the vulcanizates without phosphite.

In another group of experiments, ethyl acrylate was polymerized with 5% of acrylonitrile plus various amounts of beta chloroethoxy ethyl acrylate. The products were compounded with and without 1% of dibutyl

phosphite (X-149-154). The phosphite stabilized only those compositions containing low concentrations of beta chloroethoxy ethyl acrylate (less than 1%). It did not prevent embrittlement of compositions containing more than 1.5% of beta chloroethoxy ethyl acrylate when exposed to air at 350°F. for 250 hours.

A series of copolymers of ethyl acrylate and beta chloroethoxy ethyl methacrylate compositions (X-181-184, X-189) compounded without dibutyl phosphite remained flexible after 250 hours in air at 350°F.

c. Dibutyl Phosphite in 1, 1-Dihydroperfluorobutyl Acrylate

(PFBA)

Dibutyl phosphite (1%) did not increase the dry heat resistance of PFBA (X-170-171). It did increase the tensile strength retention of PFBA, however, after immersion for 250 hours in Penola oil at 350°F.

d. Kel F in Ethyl Acrylate-Vinyl Triethoxysilane Copolymers

Kel F powder was added to a vinyl triethoxysilane-ethyl acrylate gum rubber. The vulcanizate of this composition swelled negligibly in alkylate fuel and remained flexible after 200 hours in air at 350°F.

3. Evaluation of Fillers

A limited number of experiments were run to determine the effect of fillers on the properties of gum rubbers. Substitution of sized Hi-Sil (colloidal silica) for carbon black in compounding copolymers of ethyl acrylate and vinyl triethoxysilane resulted in no great improvement in the properties of vulcanizates. Sodium chloride (5%) was milled into a Hycar PA-21 formulation to check the effect of incomplete removal of salt during washing of the gum. There was no significant effect on the properties of the vulcanizate.

G. Vinyl Triethoxysilane Polymers

In initial screening tests, copolymers of vinyl triethoxysilane and ethyl acrylate were the most promising. Considerable work was therefore done on variations in the polymerization recipe for these gum rubbers as well as on variations in compounding.

1. Copolymers with Ethyl Acrylate

In one series, a gum containing 1% of silane was vulcanized with 2, 4, and 6% of Trimene Base. The weight loss and tensile strength after 250 hours in air at 350°F. increased and flexibility decreased with increasing concentrations of Trimene Base. After 250 hours in Penola oil at 350°F.,

the tensile strength also increased with Trimene Base concentration (190, 260, and 350 psi for 2, 4, and 6% of Trimene, respectively), but the linear swelling was unaffected.

In a second series, copolymers containing 0.5, 1.0, and 2.5% of vinyl triethoxysilane were compounded with 1% and 2% of Trimene Base. The copolymers containing 0.5 and 1.0% of vinyl triethoxysilane were moldable. Their vulcanizates were strong and flexible after 24 hours at 350°F. in an air oven and had weight losses of 2 to 3%. After immersion for 72 hours in Penola oil at 350°F. the vulcanizates swelled 23-62% but retained their flexibility and strength. Copolymers containing 2.5% of vinyl triethoxysilane set prematurely and had poor molding characteristics.

Copolymers containing 0.5% of silane were compounded with and without 1% of sulfur to determine whether sulfur retarded degradation or overcure. Trimene Base in 2% concentration was used as the vulcanizer. The sulfur-free samples retained their flexibility better than sulfur-containing samples on air exposure but swelled more after immersion in alkylate fuel or Penola oil. The tensile strengths were practically equivalent.

Increasing the Trimene Base concentration to 4% in sulfur-containing samples increased the tensile strength by 100% after 250 hours in air at 350°F. and also increased the flexibility. The swelling in Penola oil and alkylate fuel was increased but the tensile strength retention after immersion was unaffected. Substitution of Silene L (colloidal silica) for Philblack O lowered the initial tensile strength and also the tensile strength retention after immersion in alkylate fuel.

Vinyl triethoxysilane (0.5%) was copolymerized with ethyl acrylate in the presence of 0.04%, 0.025%, and 0% of 3B mercaptan and vulcanized. The properties of the vulcanizates improved with decrease in mercaptan concentration. For example, after exposure to air at 350°F. for 250 hours, the weight losses were 19.5%, 16%, and 14.5%, in order of decreasing mercaptan content, and only the sample containing no mercaptan remained flexible. Tensile strength values after immersion in Penola oil at 350°F. for 250 hours were 300, 320, and 400 psi in the same order as above.

2. Terpolymers With Ethyl Acrylate and Acrylonitrile

A series of terpolymers of ethyl acrylate with 10% of acrylonitrile and 2 to 5% of vinyl triethoxysilane were compounded with 1% of dibutyl phosphite. Only the sample containing 3% of vinyl triethoxysilane remained flexible after 250 hours in air at 350°F. After 250 hours in Penola oil at 350°F., the linear swelling for the various samples ranged from 0.5 to 4.5% and the tensile strength ranged from 570 to 1,610 psi. The minimum tensile strength was attained with 3% of vinyl triethoxysilane, but the maximum was reached at concentrations both above and below 3%. The sample containing 5% of vinyl triethoxysilane became brittle after immersion in Penola oil.

Contrails

In another group of experiments, vinyl triethoxysilane (0.5%) and ethyl acrylate were polymerized with 1 to 10% of acrylonitrile in the presence of 0.05% of 3B mercaptan and with no mercaptan. As expected, the acrylonitrile reduced the swelling in solvents and improved the heat resistance of vulcanizates made from these polymers, but decreased the flexibility after heating. A sample containing 1% of acrylonitrile remained flexible after 250 hours in air at 350°F.; a similar sample containing 5% of acrylonitrile became brittle. Elimination of mercaptan from the polymerization recipe led to better tensile strength retention but poorer aging characteristics in air at 350°F.

Other terpolymers of vinyl triethoxysilane (0.5%) and ethyl acrylate with 5 and 10% of acrylonitrile were compounded with the usual fillers plus 1% of dibutyl phosphite. All vulcanizates were flexible after 250 hours in air at 350°F. The tensile strength retention increased with acrylonitrile concentration. The best sample of this series had a gum rubber base composed of 0.5% of vinyl triethoxysilane, 10% of acrylonitrile, and 89.5% of ethyl acrylate. This base was compounded with 20% of Philblack O, 2% of Trimene Base, 1% of dibutyl phosphite, and 1% of stearic acid. After 250 hours in air at 350°F. the tensile strength of the vulcanizate was 1,340 psi; after 250 hours in Penola oil at 350°F. it was 1,050 psi. The heated specimens were very flexible.

3. Copolymers With Other Acrylates and Methacrylates

Vinyl triethoxysilane was also copolymerized with the following acrylates and methacrylates, but all the copolymers were unsatisfactory as gum rubber bases.

a. n-Butyl Acrylate

Copolymers of n-butyl acrylate with vinyl triethoxysilane were soft and had poor properties after compounding.

A gum containing 1% of vinyl triethoxysilane was very flexible. Since very little Santomerse B could be washed out, the latter was probably soluble in the gum and acted as a plasticizer. This gum was compounded with 2% of Trimene Base and vulcanized. The vulcanizate increased in tensile strength from 160 to 620 psi after 250 hours in air at 350°F. but became brittle. It swelled excessively and almost completely lost its tensile strength after immersion in alkylate fuel or Penola oil.

A copolymer of n-butyl acrylate with 1% of vinyl triethoxysilane was compounded with dibutyl phosphite. The vulcanizate became brittle after heating in air at 350°F., swelled excessively in alkylate fuel, and melted after 250 hours in Penola oil at 350°F.

Continued

b. 2-Ethylhexyl Acrylate

The 2-ethylhexyl acrylate copolymers were soft and had poor properties after compounding.

c. Ethyl Methacrylate

The copolymer was hard and was not compounded.

d. Lauryl Methacrylate

A viscous oil was produced that did not stiffen after two hours in contact with boiling water.

e. n-Butyl Methacrylate

A hard, tough solid was produced. It lacked flexibility and when compounded with 20% of Philblack O and 2% of Trimene Base, it became brittle.

f. n-Hexyl Methacrylate

A semi-solid wax was produced. It did not solidify after two hours in contact with boiling water.

g. Methyl Acrylate

The gum possessed very little flexibility and became stiff after compounding.

h. Mixtures (50-50) of Ethyl Acrylate With n-Butyl Methacrylate, Methyl Acrylate, or Methyl Methacrylate

These compositions were too stiff for use as elastomers.

4. Additional Compositions Screened

The compositions and properties of an additional series of vulcanizates prepared from vinyl triethoxysilane polymers are given in Tables 3 and 4. The gum rubbers used were mainly terpolymers of vinyl triethoxysilane, ethyl acrylate, and acrylonitrile. They were compounded with Philblack O, Trimene Base, stearic acid and/or Kel F powder. Stearic acid tended to increase the swelling of vulcanizates in solvents. Kel F powder, however, again showed promise as an additive for reducing swelling as well as for maintaining flexibility when heated.

TABLE NO. 3
COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)				Gum Rubber
		Phylblack O	Trimene Base	Other Additives		
A-5091-1	Ethyl acrylate (44.5); vinyl triethoxy silane (0.5); acrylonitrile (5.0)	7.0	1.0	Stearic Acid (0.28) Kel F (4.0)	28	
A-5091-2A	Ethyl acrylate (44.5); vinyl triethoxy silane (0.5); acrylonitrile (5.0); Kel F Oil (1.0)	5.25	0.75	Stearic Acid (0.21) Kel F (3.0)	21	
A-5091-2B	Ethyl acrylate (44.5); vinyl triethoxy silane (0.5); acrylonitrile (5.0); Kel F Oil (1.0)	6.0	1.25	Kel F (6.0)	21	
A-5091-3	Ethyl acrylate (44.5); vinyl triethoxy silane (0.5); acrylonitrile (5.0); Kel F Oil (2.0)	10.0	1.43	Kel F (5.7)	40	
A-5091-4	Ethyl acrylate (44.5); vinyl triethoxy silane (0.5); acrylonitrile (5.0); Kel F Oil (8.0)	17.0	1.43	Kel F (5.7)	40	
A-5088	Ethyl acrylate (44.5); acrylonitrile (5.0); vinyl ethyl diethoxy silane (0.5)	10.4	1.1	Stearic Acid (0.52)	40	
A-5089	Ethyl acrylate (44.5); acrylonitrile (5.0)	10.0	1.43	Kel F (5.7)	40	

Contracts

TABLE NO. 3 (Cont'd)
COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)			
		Philtack O	Trimene Base	Other Additives	Gum Rubber
A-5095-1	Ethyl acrylate (42); acrylonitrile (7.5); vinyl triethoxy silane (0.5)	10.0	0.21	Kel F (10.0)	40
A-5095-2	Ethyl acrylate (42); acrylonitrile (7.5); vinyl triethoxy silane (0.5)	10.0	1.5	Kel F (10.0)	40
A-5095-3	Ethyl acrylate (41.25); acrylonitrile (7.5); vinyl triethoxy silane (0.75)	10.0	0.21	Kel F (10.0)	40
A-5095-4	Ethyl acrylate (41.25); acrylonitrile (7.5); vinyl triethoxy silane (0.75)	10.0	2.14	Kel F (10.0)	40
A-5092-5	Methyl acrylate (45); acrylonitrile (9.0); vinyl triethoxy silane (0.5)	0	1.07	Kel F (28.6)*	40
A-5092-4	Ethyl acrylate (44.5); acrylonitrile (5.0); vinyl triethoxy silane (0.5)	10.0	0	Kel F (10.0)*	40
A-5092-2	Ethyl acrylate (42); vinyl triethoxy silane (0.5); acrylonitrile (7.5)	10.0	0	Kel F (10.0)	40
A-5092-1	Ethyl acrylate (42); vinyl triethoxy silane (0.5); acrylonitrile (7.5)	10.0	0.211	Kel F (10.0)	40

* Kel F powder was mixed with some of the Trimene Base before addition.

TABLE NO. 4

PROPERTIES OF VULCANIZATES

Sample No	Original Tensile Strength (psi)	250 hr. Exposure to Air at 350°F			72 hr. Immersion in 70-30 Iso-octane-Toluene at 65° F		250 hr. Immersion in Penola Oil at 350°F		
		% Wt. Loss	180° Bend	Tensile Strength (psi)	% Linear Swelling	Tensile Strength	% Linear Swelling	180° Bend	Tensile Strength (psi)
A-5091-1	1421	6.4	O.K.; S.C.*	919	5.8	653	4.3	O.K.	1111
A-5091-2A	1265	6.0	O.K.	670	5.8	467	5.7	O.K.	1058
A-5091-2B	1424	5.9	O.K.	1084	5.0	663	2.8	O.K.	1364
A-5091-3	1231	5.4	O.K.	864	5.0	590	5.0	O.K.	1318
A-5091-4	1126	5.1	O.K.	1087	5.8	621	2.8	O.K.	1249
A-5088	2031	6.1	O.K.	1119	7.2	735	8.0	O.K.	1058
A-5089	1305	4.3	O.K.	1282	6.4	693	4.3	O.K.	1129
A-5095-1	819	2.6	O.K.	1048	1.4	112	0	O.K.	659
A-5095-2	1289	5.0	O.K.	1714	2.2	341	2.1	O.K.; Stiff	1714
A-5095-3	1219	1.9	O.K.	1383	0.7	755	- 2.1	Good	1313
A-5095-4	932	6.4	O.K.	1091	2.2	326	0.7	O.K.	1399
A-5092-5	Not Suitable for Testing; Too Brittle								
A-5092-4	817	5.7	O.K.	682	5.9	359	2.2	O.K.	954
A-5092-2	1196	1.6	O.K.	1393	1.4	578	- 1.4	O.K.	1297
A-5092-1	1600	2.1	O.K.	1408	1.4	935	- 4.6	Good	1280

Notes: *S.C. = Surface Cracks.

All data on heated or immersed samples are the average of three samples. In the 180° bend test, if all three samples were not identical, the divergent results are indicated.

IV. VINYL TRIETHOXYSILANE - ETHYL ACRYLATE COPOLYMERS

In the screening tests, the gum rubbers containing ethyl acrylate and vinyl triethoxysilane showed the most promise from the standpoint of thermal and solvent resistance. Table No. 5 lists variations of all the best compositions containing vinyl triethoxysilane. The properties of the vulcanizates prepared from these compositions are listed in Table No. 6. Acrylon BA-12 and EA-5, two acrylic rubbers manufactured by American Polymer Corporation, are included in these tables for comparison.

Two experimental designs were carried out to determine the optimum concentration of dibutyl phosphite or Kel F powder for maintaining the flexibility of vulcanizates of vinyl triethoxysilane-ethyl acrylate gum rubbers when heated in air or Penola oil at 350°F. Tests were performed to determine if the vulcanizates possessed any significant low-temperature resistance. Long-time aging tests were performed on the optimum compositions.

A short theoretical investigation was also conducted on the cross-linking mechanism of acrylate-vinyl alkoxysilane copolymers.

A. Experimental Designs With Dibutyl Phosphite and Kel F

The inclusion of acrylonitrile in the polymerization recipe for ethyl acrylate-vinyl triethoxysilane gum rubbers produced polymers that swelled very little in 70-30 iso-octane-toluene and Penola oil. However, to maintain the flexibility of these rubber compositions when heated in air or Penola oil at 350°F., they had to be compounded with dibutyl phosphite or Kel F powder.

An experimental design was carried out with each additive to determine the optimum concentration with respect to the concentrations of three other variables:

- (a) Trimene Base
- (b) Philblack O
- (c) Acrylonitrile.

The compositions and properties of the vulcanizates containing Kel F are listed in Tables 7 and 8. The compositions and properties of the vulcanizates containing dibutyl phosphite are listed in Tables 9 and 10.

TABLE NO. 5

COMPOSITION OF BEST VINYL TRIETHOXSILANE -
ETHYL ACRYLATE VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)				Gum Rubber
		Philblack O	Trimene Base	Kel F	Other Additives	
A-5096-1	Vinyl triethoxy silane (0.75); Ethyl acrylate (41.75); acrylonitrile (7.5)	7.8	0	0	0	31
A-5096-3	Vinyl triethoxy silane (1.5); Ethyl acrylate (41); acrylonitrile (7.5)	10.0	0.21	10.0	0	40
A-5096-4	Vinyl triethoxy silane (0.75); Ethyl acrylate (39.25); acrylonitrile (10)	9.0	0.21	9.0	0	36
XX-9	Vinyl triethoxy silane (0.75); Ethyl acrylate (41.75); acrylonitrile (7.5)	27.0	0	0	0	54
XX-10	Vinyl triethoxy silane (0.75); Ethyl acrylate (49.25)	8.5	0	8.5	0	34
XX-11	Vinyl ethyl diethoxy silane (0.75); acrylonitrile (7.5); ethyl acrylate (41.5)	7.0	0	7.0	0	28
XX-12	Vinyl phenyl diethoxy silane (0.75); acrylonitrile (7.5); Ethyl acrylate (41.5)	10.5	0	10.5	0	42
XX-13	Vinyl triethoxy silane (0.75); acrylonitrile (7.5); Ethyl acrylate (41.75)	0	0	10.0	Silene L (10)	40
XX-14	Vinyl triethoxy silane (0.75); Ethyl acrylate (49.25)	0	0	6.8	Magnesium methacrylate (6.8)	27.3

TABLE NO. 5 (Cont'd)
COMPOSITIONS OF BEST VINYL TRIETHOXSILANE
ETHYL ACRYLATE VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)					Gum Rubber
		Philblack O	Trimene Base	Kel F	Other Additives	Rubber	
XX-15	Vinyl triethoxy silane (0.75); Ethyl acrylate (49.25)	0	0.21	6.8	Magnesium Methacrylate (6.8)	27.3	
XX-16	Ethyl acrylate (42.5); acrylonitrile (7.5)	10.0	0	10.0	0	40	
XX-17	Ethyl acrylate (42.5); acrylonitrile (7.5)	0	0	8.75	Magnesium Methacrylate (8.75)	35	
XX-18	Vinyl triethoxy silane (0.75); ethyl acrylate (41.75); acrylonitrile (7.5)	6.0	1.0	0	Dibutyl Phosphite (0.42)	42	
XX-19	Acrylon BA-12	25.0	0.5	0	Sulfur (0.5) Stearic Acid (0.5)	50	
XX-20	Acrylon EA-5	25.0	0.75	0	Sulfur (0.5) Stearic Acid (0.5)	50	

TABLE NO. 6

PROPERTIES OF BEST VINYL TRIETHOXSILANE-

ETHYL ACRYLATE VULCANIZATES

Sample No.	Original Tensile Strength (psi)	250 hr. Exposure to Air at 350° F			72 hr. Immersion in 70-30 Iso-octane-Toluene at 65° F		250 hr. Immersion in Penola Oil at 350° F		
		% Wt. Loss	180° Bend	Tensile Strength (psi)	% Linear Swelling	Tensile Strength (psi)	% Linear Swelling	180° Bend	Tensile Strength (psi)
A-5096-1	542	7.4	B.*	- - -	6.6	39	1.4	B.	- - -
A-5096-3	1289	3.3	O.K.	Strong; 800	1.4	498	3.6	B.	- - -
A-5096-4	1669	3.2	O.K.	Strong; 800	0.7	1279	2.1	B.	- - -
XX-3	1263	4.4	O.K.	Strong; 800	2.1	385	-5.1	O.K.	- - -
XX-8	1389	4.6	O.K.	Strong; 800	0	596	-6.5	B.	- - -
XX-9	1407	4.0	B.	- - -	1.4	1024	0	Stiff	- - -
XX-10	554	9.4	B.	- - -	8.2	0	10.0	B.	- - -
XX-11	373	4.8	O.K.	Replaced**	2.2	0	2.1	B.	- - -
XX-12	370	4.7	O.K.	Replaced**	3.6	0	1.4	B.	- - -
XX-13	823	5.9	B.	- - -	4.3	219	2.2	O.K.	651
XX-14	794	16.9	B.	- - -	6.4	275	6.4	O.K.	499
XX-15	339	16.9	B.	- - -	5.7	125	6.4	O.K.	Weak
XX-16	243	5.6	O.K.	Replaced	2.1	0	0.7	B.	- - -
XX-17	1015	11.4	B.	- - -	2.8	101	3.6	O.K.	902
XX-18	952	8.8	O.K.	Replaced	6.5	457		Replaced	
XX-100	946	5.2	O.K.	Replaced	2.2	237		Replaced	
XX-19	271	-	O.K.	Replaced	2.8	Weak	40.0	O.K.	Replaced
XX-20	1051	-	O.K.	Replaced	8.5	780	7.8	O.K.	Replaced

Notes: * B. = Brittle

** Samples marked "Replaced" were still flexible at the end of 250 hours and were replaced in the test exposures for long-range tests (up to 1000 hours).

TABLE NO. 7
EXPERIMENTAL DESIGN WITH SAMPLES CONTAINING KEL F

COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (grams)	Vulcanizate Composition (grams)			
		Philblack O	Kel F	Trimene Base	Gum Rubber
A-5090-A	Ethyl acrylate (49.5); vinyl triethoxy silane (0.5)	1	1	0	28
A-5090-B	Same as A-5090-A	7	7	0.36	28
A-5090-C	Same as A-5090-A	2	4	0.75	28
A-5090-D	Same as A-5090-A	4	10	1.5	28
A-5090-E	Ethyl acrylate (47); acrylonitrile (2.5); vinyl triethoxy silane (0.5)	7	10	0	28
A-5090-F	Same as A-5090-E	1	4	0.36	28
A-5090-G	Same as A-5090-E	4	7	0.75	28
A-5090-H	Same as A-5090-E	2	1	1.5	28
A-5090-I	Ethyl acrylate (44.5) acrylonitrile (5.0); vinyl triethoxy silane (0.5)	2	7	0	28
A-5090-J	Same as A-5090-I	4	1	0.36	28
A-5090-K	Same as A-5090-I	1	10	0.75	28
A-5090-L	Same as A-5090-I	7	4	1.5	28
A-5090-M	Ethyl acrylate (42); acrylonitrile (7.5); vinyl triethoxy silane (0.5)	4	4	0	28
A-5090-N	Same as A-5090-M	2	10	0.36	28
A-5090-O	Same as A-5090-M	7	1	0.75	28
A-5090-P	Same as A-5090-M	1	7	1.5	28

TABLE NO. 8

EXPERIMENTAL DESIGN WITH SAMPLES CONTAINING KEL FPROPERTIES OF VULCANIZATES

Sample No.	Original Tensile Strength (psi)	250 hr. Exposure to Air at 350°F			72 hr. Immersion in 70-30 Iso-octane-Toluene at 65° F		250 hr. Immersion in Penola Oil at 350° F		
		% Wt. Loss	180° Bend	Tensile Strength (psi)	% Linear Swelling	Tensile Strength (psi)	% Linear Swelling	180° Bend	Tensile Strength (psi)
A-5090-A	276	9.0	O.K.	210	14.0	79	14.2	O.K.	130
A-5090-B	823	6.0	S.C.*	430	10.0	330	9.9	C.K.	304
A-5090-C	288	8.0	S.C.	238	11.5	144	16.6	O.K.	293
A-5090-D	519	6.0	O.K.	346	8.0	220	9.9	O.K.	396
A-5090-E	736	2.0	O.K.	541	3.5	292	0	O.K.	537
A-5090-F	377	4.0	S.C.	304	9.5	91	7.9	O.K.	190
A-5090-G	590	6.0	S.C.	366	7.0	223	4.2	O.K.	546
A-5090-H	595	10.0	O.K.	1054	9.5	198	7.9	O.K.	600
A-5090-I	492	5.0	O.K. Stiff	403	5.0	244	0	O.K.	454
A-5090-J	786	7.0	B**	432	7.0	385	6.5	O.K.	694
A-5090-K	216	8.0	B	364	7.0	90	3.6	O.K.	275
A-5090-L	780	5.5	O.K. Stiff	859	6.0	388	4.2	O.K.	984
A-5090-M	431	2.5	O.K. Stiff	918	3.0	148	0	O.K.	475
A-5090-N	645	4.0	O.K. Stiff	781	3.5	424	3.6	O.K.	704
A-5090-O	1190	5.5	B	861	2.0	1000	3.6	O.K.	1370
A-5090-P	326	7.0	B	774	3.5	209	2.9	O.K.	1010

Notes: * S. C. = Surface Cracks.

** B = Brittle.

All data on immersed or heated samples are the average of three samples. In the 180° bend test, if all three samples were not identical, the divergent results are indicated.

TABLE NO. 9
EXPERIMENTAL DESIGN WITH SAMPLES CONTAINING DIBUTYL PHOSPHITE
COMPOSITION OF VULCANIZATES

Sample No.	Gum Rubber Composition (Grams)	Vulcanizate Composition (Grams)			
		Phillblack O	Trimene Base	Dibutyi Phosphite	Gum Rubber
A-5099-1	Ethyl acrylate (49.5); vinyl triethoxy silane (0.5)	1	0	0.028	28
A-5099-2	Same as A-5099-1	7	0.14	0	28
A-5099-3	Same as A-5099-1	2	0.75	0.84	28
A-5099-4	Same as A-5099-1	4	1.5	0.28	28
A-5099-5	Ethyl acrylate (47); acrylonitrile (2.5); vinyl triethoxy silane (0.5)	7	0	0.28	28
A-5099-6	Same as A-5099-5	1	0.14	0.84	28
A-5099-7	Same as A-5099-5	4	0.75	0	28
A-5099-8	Same as A-5099-5	2	1.5	0.028	28
A-5099-9	Ethyl acrylate (44.5); acrylonitrile (5.0); vinyl triethoxy silane (0.5)	2	0	0	28
A-5099-10	Same as A-5099-9	4	0.14	0.028	28
A-5099-11	Same as A-5099-9	1	0.75	0.28	28
A-5099-12	Same as A-5099-9	7	1.5	0.84	28
A-5099-13	Ethyl acrylate (42); acrylonitrile (7.5); vinyl triethoxy silane (0.5)	4	0	0.84	28
A-5099-14	Same as A-5099-13	2	0.14	0.28	28
A-5099-15	Same as A-5099-13	7	0.75	0.028	28
A-5099-16	Same as A-5099-13	1	1.5	0	28

TABLE NO. 10

EXPERIMENTAL DESIGN WITH SAMPLES CONTAINING DIBUTYL PHOSPHITE

PROPERTIES OF VULCANIZATES

Sample No.	Original Tensile Strength (psi)	250 Hr. Exposure to Air at 350° F		72 Hr. Immersion in 70-30 Iso-octane-Toluene at 65° F		250 Hr. Immersion in Penola Oil at 350° F			
		% Wt. Loss	180° Bend	Tensile Strength (psi)	% Linear Swelling	Tensile Strength (psi)	% Linear Swelling	180° Bend	Tensile Strength (psi)
A-5099-D-1	0	Melted	- - -	- - -	Too Weak	0	27.7	Too Weak	0
A-5099-D-2	156	9.5	O.K.	96	13.9	27	20.3	O.K.	0
A-5099-D-3	342	7.7	O.K.	154	14.7	86	18.6	O.K.	57
A-5099-D-4	440	12.9	O.K.	278	10.6	77	12.2	O.K.	159
A-5099-D-5	34	4.4	O.K.	450	13.4	0	9.9	O.K.	69
A-5099-D-6	62	Melted	- - -	- - -	Too Weak	0	- - -	- - -	0
A-5099-D-7	512	18.0	B*	- - -	10.8	105	8.7	O.K.	129
A-5099-D-8	289	29.3	B	- - -	10.6	52	8.9	O.K.	162
A-5099-D-9	120	10.9	O.K.	Melted	11.5	0	2.1	O.K.	100
A-5099-D-10	206	7.6	O.K.	303	7.9	31	7.8	O.K.	143
A-5099-D-11	159	9.4	O.K.	264	8.8	40	7.9	O.K.	243
A-5099-D-12	483	11.3	O.K.	725	6.4	101	4.3	B	561
A-5099-D-13	229	13.0	B	- - -	1.4	32	4.2	B	B
A-5099-D-14	236	6.6	O.K.	1212	2.2	34	2.1	O.K.	604
A-5099-D-15	628	9.7	B	- - -	5.7	287	4.3	O.K.	652
A-5099-D-16	262	24.1	B	- - -	11.7	35	3.6	O.K.	224

Notes: * B = Brittle

All data on immersed or heated samples are the average of three samples.

Continued

The data were analyzed by the method of Greco-Latin squares with each variable at the four level. The best compositions for each additive were:

(a) For Kel F powder, gum rubber polymerized as

84% ethyl acrylate
15% acrylonitrile
1% vinyl triethoxysilane

and compounded as

71.0% gum rubber
14.5% Philblack O
14.5% Kel F powder.

(b) For dibutyl phosphite, gum rubber polymerized as

89.5% ethyl acrylate
10.0% acrylonitrile
0.5% vinyl triethoxysilane

and compounded as

76.0% gum rubber
20.0% Philblack O
2.0% Trimene Base
1.0% stearic acid
1.0% dibutyl phosphite.

B. Low Temperature Properties

All available samples were tested for "cold break" at 0°F., -25°F., and -80°F. No exceptional resistance to low temperatures was noted.

Three samples were flexible at -25°F. but had very poor swelling and strength characteristics. Only one of these contained a copolymer of vinyl triethoxysilane and ethyl acrylate (A-5099-D-7, Tables 9 and 10). The other two were copolymers of vinyl triethoxysilane with 2-ethylhexyl acrylate and n-butyl acrylate, respectively.

C. Long Range Tests

Samples which remained flexible after 250 hours in air or Penola oil at 350°F. were exposed for long range tests up to 1000 hours.

No vulcanizate samples remained flexible after 1000 hours in Penola oil at 350°F. One sample (A-5099-D-3, Tables 9 and 10), consisting of vinyl triethoxysilane-ethyl acrylate gum rubber compounded with 3% of dibutyl phosphite, remained flexible after 1000 hours in air at 350°F. However, its original properties were poor and it melted in Penola oil at 350°F. Its tensile strength after 1000 hours in air at 350°F. was approximately 300 psi.

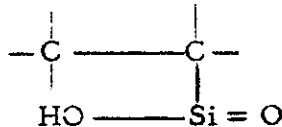
Conclusions

With the exception of the sample mentioned above, the maximum duration of flexibility (up to 750 hours) in the long range tests was obtained with samples of the best composition type determined in the experimental design with Kel F (p.33). The samples hardened progressively as the exposure continued.

D. Cross-Linking Mechanism of Vinyl Alkoxysilanes

Vinyl ethyl diethoxysilane and vinyl phenyl diethoxysilane were synthesized (see Appendix C) for use in a theoretical investigation of the cross-linking mechanism of vinyl alkoxysilanes. When used in 1% concentration, these silanes increased the swelling in solvents and the brittleness of ethyl acrylate gum rubbers.

As a working hypothesis, we assume that in water emulsion vinyl triethoxysilane first hydrolyzes and then dehydrates within itself, so that it ends up in the copolymer as



This leaves only one hydroxyl group available for cross-linking. The diethoxysilanes, however, hydrolyze but do not dehydrate within themselves. Thus, two hydroxyl groups are available for cross-linking.

In addition, we assume the following:

- (a) That the rates of reaction of the diethoxysilanes and the triethoxysilane towards ethyl acrylate are approximately equal.
- (b) That the solubilities of the diethoxysilanes and the triethoxysilane in ethyl acrylate and in water are approximately equal.

If these assumptions are true we may also assume that the copolymer of ethyl acrylate with vinyl triethoxysilane will have a lower softening point than the copolymers of ethyl acrylate with the diethoxysilanes, theoretically due to the presence of fewer cross-links.

The softening points of the copolymers of ethyl acrylate with vinyl triethoxysilane, vinyl ethyl diethoxysilane, and vinyl phenyl diethoxysilane were determined for samples containing equal molar quantities of silane:

Concentration %	Softening Point (°C.)		
	Vinyl Triethoxysilane	Vinyl Ethyl Diethoxysilane	Vinyl Phenyl Diethoxysilane
0.10	110	115	115
0.25	115	120	120
0.50	120	120	120

Dry copolymers of ethyl acrylate and 5% of vinyl triethoxysilane, prepared in carbon tetrachloride or heptane solution rather than water emulsion, did not contain hydroxyl groups, as shown by infrared spectrograms. The softening points of these materials were less than 100°C., indicating that no cross-linking occurred.

V. CONCLUSIONS AND RECOMMENDATIONS

The best gum rubber compositions developed on this project are based on copolymers of ethyl acrylate and vinyl triethoxysilane. For optimum properties with respect to thermal and solvent resistance, the following recommendations are made:

- (a) For minimum swelling in 70-30 iso-octane-toluene and Penola oil at 350°F., acrylonitrile must be included in the gum rubber. Organic vulcanizing aids such as excess amine (Trimene Base) and stearic acid, however, tend to increase swelling.
- (b) For minimum weight loss after heating in air at 350°F., it is desirable to vulcanize vinyl triethoxysilane-ethyl acrylate gum rubbers containing Kel F without amine or sulfur.
- (c) For maintaining the flexibility of vulcanizates heated in air or Penola oil, either Kel F or dibutyl phosphite is effective. Kel F has no effect on either swelling in solvents or weight loss after heating.
- (d) For good original tensile strength and for good tensile strength retention after heating in air or Penola oil at 350°F., a reinforcing filler is necessary. In this project, Philblack O was superior to other reinforcing materials.

The following types of compositions had the best overall properties:

(A)-1

Gum rubber polymerized as

84% ethyl acrylate
15% acrylonitrile
1% vinyl triethoxysilane

and compounded as

71.0% gum rubber
14.5% Philblack O
14.5% Kel F powder

(B)-1

Gum rubber polymerized as

89.5% ethyl acrylate
10.0% acrylonitrile
0.5% vinyl triethoxysilane

Contrails

and compounded as

- 76% gum rubber
- 20% Philblack O
- 2% Trimene Base
- 1% stearic acid
- 1% dibutyl phosphite

The properties of these compositions are summarized in the following table.

Composition	Original Tensile Strength (psi)	72 Hr. Immersion in 70-30 Iso-octane-Toluene at 65°F.		250 Hr. Exposure to Penola Oil at 350°F.		250 Hr. Exposure to Air at 350°F.	
		% Linear Swelling	Tensile Strength (psi)	% Linear Swelling	Tensile Strength (psi)	% Weight Loss	Tensile Strength (psi)
(A)-1	1196	1.4	578	-1.4	1297	1.6	1393
(B)-1	1120	7.5	430	6.0	652	8.0	780

In the long range tests (1000 hours in air or Penola oil at 350°F.), the maximum duration of flexibility (up to 750 hours) was obtained on compositions of type (A)-1.

Copolymers of vinyl triethoxysilane and ethyl acrylate could be vulcanized without additives through the formation of cross-linkages. The data from the theoretical investigation on vinyl alkoxysilanes indicate that cross-linking takes place through adjacent $>SiOH$ groups formed in water emulsion polymerization.

With respect to further improvement of the properties of vinyl triethoxysilane-ethyl acrylate gum rubbers, we suggest the following approaches:

- (a) Investigation of other phosphite additives, in addition to dibutyl phosphite.
- (b) Investigation of the use of phosphites in conjunction with Kel F.
- (c) Preparation of copolymers with a more uniform mer length (length of acrylate chain between vinyl triethoxysilane groups) in order to obtain increased thermal resistance.

Phosphite compounds, such as dibutyl phosphite, act as antioxidants as well as plasticizers in acrylate rubbers. In order to determine the most desirable compound for both these functions, we recommend that higher alkyl, aryl, and alkenyl phosphites be investigated as additives. High boiling aryl phosphites, in particular, because of their low evaporation rate, would be expected to be effective antioxidants at temperatures above 400°F. By copolymerizing alkenyl phosphites, such as allyl phosphite, with ethyl acrylate, antioxidants might be "built into" the polymer.

Control

The use of phosphites in conjunction with Kel F should also be investigated. Although both dibutyl phosphite and Kel F increased the flexibility of gum rubbers, it does not necessarily follow that the flexibility would be increased even more by combined use of the two additives. In work on another contract, we found that phosphites have some surface reactivity with Kel F, which might decrease their effectiveness.

The optimum length of acrylate chain between vinyl triethoxysilane groups which will give maximum thermal resistance in vinyl triethoxysilane-ethyl acrylate copolymers is unknown. No attempt was made to control mer length in the preparation of these copolymers.

The best compositions developed were prepared with approximately 1% of silane in the monomer charge. With higher concentrations of silane, the products became progressively less flexible.

If the rate of reactivity of vinyl triethoxysilane towards the growing acrylate chains is high, stepwise addition of silane might be expected to produce a more uniform mer length, resulting in increased thermal resistance. Therefore, determination of the reactivity rate is recommended.

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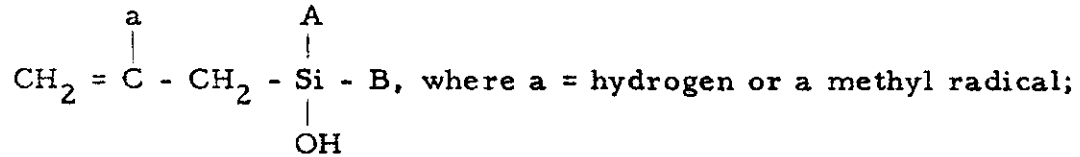
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APPENDIXES

WADC TR 54-525

50

PREPARATION OF PROPYLENE GLYCOL MONOMETHACRYLATE

Propylene glycol methacrylate (PGMM) was prepared by two methods, as follows:

Experiments KG-A, B

The following mixture was placed in a 500 milliliter one-necked, round bottom flask fitted with a reflux condenser:

- Methacrylic acid (0.5 mole)
stabilized with 0.1% hydroquinone
- 1,2-Propylene oxide (0.57 mole)
- Benzene (0.56 mole)
- Pyridine (0.0063 mole)
- Hydroquinone (0.009 mole)

The mixture was refluxed for 48 hours and the benzene removed by distillation at atmospheric pressure. The pure product was then obtained by fractional distillation at reduced pressure.

Experiments KA-482

- Glacial methacrylic acid (1 mole)
- 1,2-Propylene oxide (4 moles)
- Pyridine (0.0126 mole)
- Hydroquinone (0.018 mole)

This mixture was gently refluxed for three days. Excess propylene oxide was recovered by distillation at atmospheric pressure. The product was distilled at reduced pressure, boiling at 87°-97°C. at 6.6 millimeters.

The following table summarizes the properties of the esters prepared by the above methods.

Experiment No.	Boiling Point	Saponification No.		Yield (in %)
		Actual	Theoretical	
KG-A	96°C. at 11.5 mm.	141	144	55
KG-B	102°-104°C. at 12.5 mm.	-	144	-
KA-482 I	82°-87°C. at 6.6 mm.	185	144	-
KA-482 II	87°-97°C. at 6.6 mm.	141	144	42
KA-482 III	97°-109°C. at 6.6 mm.	121	-	-

ALPHA METHYL BETA (TRIMETHYL SILOXY) ETHYL METHACRYLATE

Alpha methyl beta (trimethyl siloxy) ethyl methacrylate was prepared as follows:

Propylene glycol monomethacrylate, 36 grams, was prepared as described in Appendix A (p. 51, KG-A, B). This monomer was mixed with one gram of hydroquinone and 28 grams of trimethyl chlorosilane in a flask equipped with a reflux condenser. After 4 hours of refluxing, the crude product was fractionated and the fraction boiling at 98-105°C. at 9 millimeters was collected. Its saponification number was 96 as compared with the theoretical value of 108.

SYNTHESIS OF VINYL SILANE COMPOUNDS

Vinyl Trimethylsilane

A solution of 81 grams (0.5 mole) of vinyl trichlorosilane in 100 ml. of absolute ether was placed in a three-necked flask fitted with a reflux condenser, a nitrogen inlet, and a dropping funnel containing 500 grams of methyl magnesium bromide. The funnel and flask were flushed continuously with dry nitrogen and the methyl magnesium bromide was introduced (three hours were required for complete addition) into the flask. The contents of the flask were then stirred for two hours, refluxed for one hour, and left in the flask overnight. After excess methyl magnesium bromide had been removed by decomposition with water and subsequent addition of dilute HCl, the ether layer was separated and added to two ether extracts of the aqueous layer. The resultant ethereal solution was fractionated with a heated column packed with glass helices. The fraction boiling at 54°-55°C. (760 mm.) had the following properties:

$$n_D^{25} = 1.3841 - 1.3877$$

$$\text{Density at } 20^\circ\text{C.} = 0.693 - 0.694$$

The literature (U.S. Patent 2,588,083) reports values of 1.3909 and 0.7038, respectively.

Vinyl Chloro Diethoxysilane

Vinyl chloro diethoxysilane was used in the preparation of both vinyl ethyl and vinyl phenyl diethoxysilanes. It was prepared by the following method:

Vinyl trichlorosilane (1 mole) was placed in a three-necked flask fitted with a reflux condenser, an HCl trap, and a dropping funnel containing ethanol (2 moles). The ethanol was added very slowly to the vinyl trichlorosilane in the flask. The reaction was endothermic and, therefore, the reaction mixture was heated to just above room temperature during the addition of the ethanol. The fraction boiling at 142°-145°C. (760 mm.) contained an amount of chlorine equivalent to that calculated from the theoretical formula for vinyl chloro diethoxysilane.

Vinyl Ethyl Diethoxysilane

Vinyl chloro diethoxysilane (1 mole) was placed in a two-necked round bottom flask fitted with a magnetic stirrer and a dropping funnel containing ethyl magnesium bromide (1 mole) in diethyl ether. The ethyl magnesium chloride was added very slowly (one drop per second) and with stirring to the vinyl chloro diethoxysilane in the flask. The reaction mixture was kept at 0°C. by placing the flask in an ice-water bath.

The product had the following properties:

Boiling point (760 mm.) = 148° - 152°C.
Refractive index at 20°C. = 1.4174

Vinyl Phenyl Diethoxysilane

Vinyl phenyl diethoxysilane was prepared by the same method used to prepare vinyl ethyl diethoxysilane, except that phenyl magnesium bromide was used in place of ethyl magnesium bromide.

The product had the following properties:

Boiling point (760 mm.) = 200°C.
Refractive index at 20°C. = 1.5179
Silicon content (as SiO₂) = 11.2%

(Theoretical silicon content = 12.7%)