Polyacrylic Ether-Ester Elastomers

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Compounding and physical properties are discussed for a new polyacrylic ether-ester elastomer which is marketed under the trade-mark Vyram. Vulcanizates of the product exhibit outstanding resistance to swell by a wide range of solvents and industrial functional fluids. As a result of increasingly stringent performance requirements, lubricants and functional fluids used in modern aircraft and industrial equipment have become more diversified, and no single fluid is likely to meet all requirements. It has become difficult to provide elastomeric compositions for sealants and packings which will resist the petroleum-base, phosphate ester, chlorinated hydrocarbon, and dibasic acid ester fluids. Vyram polyacrylic elastomer exhibits excellent resistance to all these fluids, and it may be used for service in the temperature range of 10-250° F. Several potential end uses, including hydraulic seals and packings, are suggested.

As the result of increasingly stringent performance requirements, lubricants and functional fluids used in modern aircraft and industrial equipment have become more diversified. Several years ago petroleum products supplied all needs, and it was not too difficult to provide elastomeric compositions for sealants and packings. Today, however, no single fluid is likely to meet all requirements. Petroleum-based products are used widely, but phosphate esters are employed where fire resistance and critical lubricity are required. Chlorinated hydrocarbons are used to give fire resistance with moderate lubricity. Dibasic acid esters are formulated into lubricants for very high temperature service, and glycol-water compositions may be used where service conditions are moderate. Elastomers suitable for use with individual fluids have been devised, but no commercial products with universal resistance were suitable for use with all of them. The problem is particularly acute where more than one type of fluid may contact the same elastomeric part – for example, in an aircraft employing conventional petroleum lubricants in accessories, dibasic acid ester lubricants in the engine, and phosphate ester fluid in hydraulic systems and accessories

This work reported was predicated upon the need for a universally solvent-resistant elastomer to fill specialty packing functions in military (2) and industrial applications. Discussions with packing manufacturers elicited the following target properties which could be used as a guide:

Ultimate tensile strength, lb./sq.inch	1000 (Minimum)
Elongation, %	200 (Minimum)
Hardness (Shore A)	50-80
Compression set, % (Method B)	40 (Maximum)
Solvent swell, %	-2 to 30

The testing methods are those outlined in the standard A.S.T.M. procedures. References to specific A.S.T.M. tests are given in Table I. The per cent swelling is determined by measuring the volume increase of an elastomer after immersion in a given fluid at the normal operating temperature of the fluid under actual use conditions.

This article introduces a polyacrylic ether-ester elastomer which exhibits unusual swelling resistance to a wide spectrum of solvents and functional fluids. This product is now marketed under the trade-mark Vyram (Superseding Code No. N-5400, Monsanto Chemical Co.). Compounding information and physical properties which have been measured to date are discussed. Potential end uses are suggested.

Vyram polyacrylic elastomer is polymerized from its monomer in an emulsion-type system. A bisulfite-persulfate redox catalyst is utilized to effect the polymerization.

TABLE I. TEST METHODS

Stress-strain	ASTM D412-51T
Tear strength	ASTM D624-48, Die C
Compression set	ASTM D395-53T, Method B
Oven air aging	ASTM D573-53
Solvents resistance	ASTM D471-54
Low temperature flexibility	ASTM D736-46T ASTM D1053-52T
Electrical resistivity	ASTM D99-48T
Ozone resistance	Dynamic Method (3) Static Method: bent loop, conditions are used in dynamic method.

A latex of 20% solids concentration is obtained in the process. The processing of the gum polymer, like other polyacrylic elastomers, presented some difficulties and a more readily processed material could be formed when a masterbatch containing carbon black and silica was prepared. A conductive channel black was found to be the most desirable for the improvement of the processing characteristics. Although fine furnace blacks are often considered to be superior to the conductive channel blacks as reinforcing agents for polyacrylic elastomers, little or no advantage is observed when the fine furnace blacks are used in Vyram polyacrylic elastomer.

The elastomer is currently marketed in the form of a masterbatch with carbon black and silica. The composition of the product is as follows:

	Parts by Weight
Polymer	100
Conductive channel black	30
Silica	10
Oleic acid	1
Total	141

Room temperature stability tests on the masterbatch have shown no change in properties over a 12-month period.

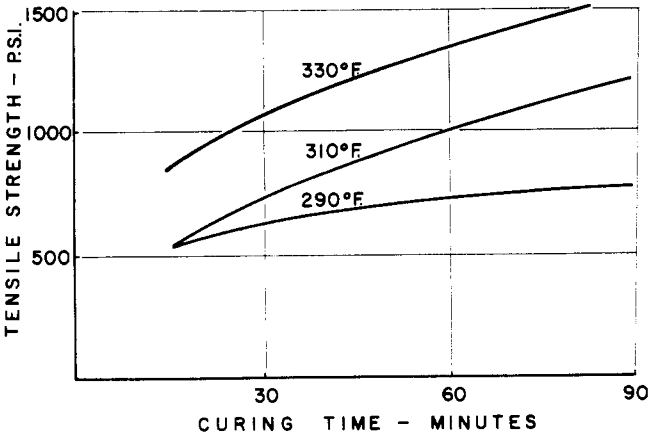

Figure 1. Tensile strength versus time and temperature of cure

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TABLE II. SUMMARY OF PROPERTIES OF VYRAM POLYACRYLIC ELASTOMER WITH VARIOUS CURATIVE SYSTEMS

	Stocks						
	1	2	3	4	5	6	7
Vyram masterbatch	141.0	141.0	141.0	141.0	141.0	141.0	141.0
Magnesuim oxide	20.0	...	...	...	...	...	...
Zinc oxide	...	...	...	...	5.0	...	...
Lead dioxide (plattnerite)	5.0	...	...	...	...	...	...
Triethylenetetramine	...	1.5	3.0	3.0	...	...	...
Sulfur	...	...	...	1.0	...	...	...
GMF	...	...	...	...	5.0	...	...
Lead oxide, red (minium)	...	...	...	...	5.0	...	...
Benzoyl peroxide	...	...	...	...	...	5.0	...
Sodium metasilicate, $9H_2O$	...	...	...	...	...	...	9.0
Calcium hydroxide	...	...	...	...	...	...	4.0
Stearic acid	3.0	1.0	1.0	1.0	3.0	...	...
Cure min. at 330° F.	60	120	60	60	240	320	30
Hardness, Shore "A"	72	58	65	60	82	47	58
300% modulus, lb./sq. inch	1183	340	996	366	...	490	...
Tensile, lb./sq. inch	1183	663	1016	736	1316	580	936
Elongation, %	300	610	306	510	286	423	246
Tear, lb./inch	192	110	126	97	198	95	106
Compression set, method B							
70 hr. at 212° F.	88	84	77	86	83	72	86
70 hr. at 212° F. (tempered 24 hr. at 300° F.)	60	31	36	31	a	17	a
Low temperature flexibility							
Pass	-10° C. (+14° F.)	-10° C. (+14° F.)	-10° C. (+14° F.)	-10° C. (+14° F.)	-10° C. (+14° F.)	-10° C. (+14° F.)	-5° C. (+23° F.)
Fail	-15° C. (+5° F.)	-15° C. (+5° F.)	-15° C. (+5° F.)	-15° C. (+5° F.)	-15° C. (+5° F.)	-15° C. (+5° F.)	-10° C. (+5° F.)

[a] Shattered under compression.

TABLE III. OXIDE CURING SYSTEMS

	Stocks							
	1	2	3	4	5	6	7	8
Vyram masterbatch	141	141	141	141	141	141	141	141
Magnesium oxide	...	...	10	15	20	20	15	20
Lead dioxide (plattnerite)	5	15	5	5	5	2.5	2.5	...
Stearic acid	3	3	3	3	3	3	3	3
Cure min. at 330° F.	60	60	60	60	60	60	60	60
Hardness, Shore A	61	76	69	73	78	70	68	61
300% modulus, lb./sq. inch	340	1226	650	990	1156	740	656	216
Tensile strength, lb./sq. inch	443	1310	776	1043	1156	786	703	243
Elongation, %	866	346	510	386	326	420	513	1073

TABLE IV. POLYAMINE CURING SYSTEMS

	Stocks								
	1	2	3	4	5	6	7	8	9
Vyram masterbatch	141	141	141	141	141	141	141	141	141
Stearic acid	1	1	1	1	1	1	1	1	1
Triethylenetetramine	1	2	3	...	...	...	...	...	...
Diethylenetriamine	...	...	...	1	2	3	...	...	...
Tetraethylenepentamine	...	...	...	...	...	...	1	2	3
Cure at 330° F.	60	60	60	60	60	60	60	60	60
Hardness	a	62	65	a	60	70	a	65	72
Modulus, 300%	a	206	683	a	223	913	a	153	873
Tensile	a	483	796	a	436	913	a	360	906
Elongation	a	670	343	a	556	300	a	753	330

[a] Partial cure.

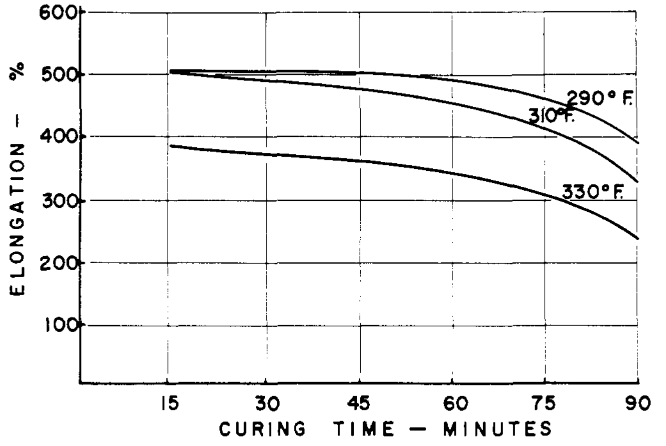

Figure 2. Elongation versus time and temperature of cure

EXPERIMENTAL

The compounding of the masterbatch was carried out on a 6 x 12 inch laboratory rubber mill. The crumb readily sheeted out on the front roll. High heat buildup during milling was characteristic, so cooling water was maintained on the rolls. Upon addition of vulcanizing ingredients, particularly metallic oxides, the stock normally shifted to the back roll, from which it could be sheeted off and blended.

In compounding for the recommended oxide cure (Vyram-141, magnesium oxide 20, lead dioxide 5, and stearic acid 3), rapid addition of magnesium oxide was carried out after adding one quarter to one half of the stearic acid. The remainder of the stearic acid was added midway through the magnesuim oxide cycle. This precaution forestalled splitting of the stock between the mill rolls. This same procedure was found to be equally effective in a Banbury mixing cycle.

The tests listed in Table I were carried out by standard A.S.T.M. methods (1), unless otherwise indicated.

VULCANIZATION

Many curative systems for saturated polyacrylic elastomers are reported in the literature. Some of these are metallic oxides (6), polyamines (7), dioximes (8), peroxides (8), and sodium metasilicate (5, 9). Table II summarizes the data obtained in studies to adapt these systems to Vyram polyacrylic elastomer.

The most promising system found is one containing a mixture of metallic oxides. Compounding studies of combinations of lead dioxide and magnesium oxide are outlined in Table III. Stock 5 in Table III in which a ratio of 20 parts of magnesium oxide to 5 parts of lead dioxide is suggested as giving the best level of properties. Higher amounts of lead dioxide can be used to give slightly better original properties, but somewhat poorer aging properties are obtained. When the amount of lead dioxide is decreased, the original properties obtained after a 60-minute press cure are poor but postcuring in an air oven raises the physical properties to an acceptable level, and an excellent aging stock is obtained. Therefore, by varying the amounts of lead dioxide and magnesium oxide the level of cure and retention of physical properties with high temperature aging can be controlled within certain limits.

Other lead oxides and basic lead salts can be used to effect a cure of Vyram polyacrylic elastomer. The level of

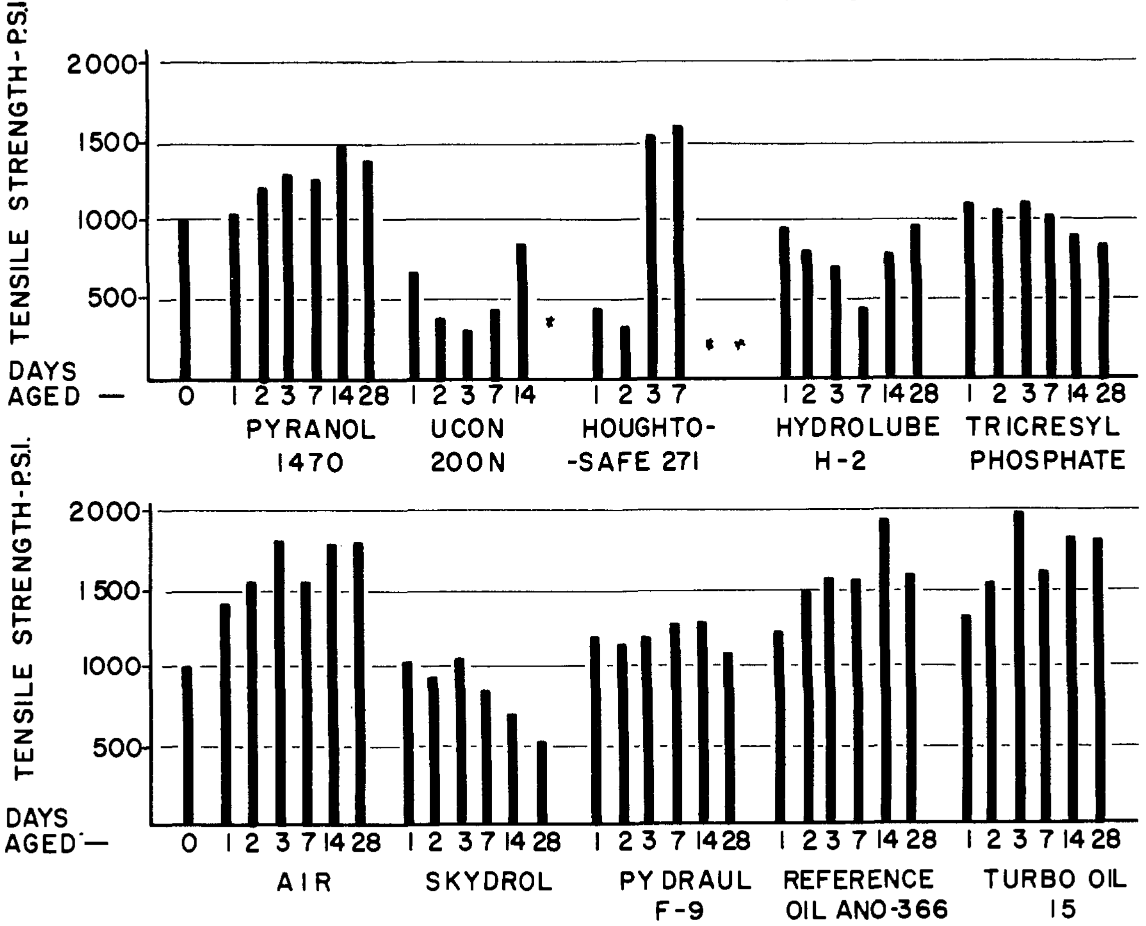

Figure 3. Changes in tensile strength with aging in air and selected fluids at 212° F.

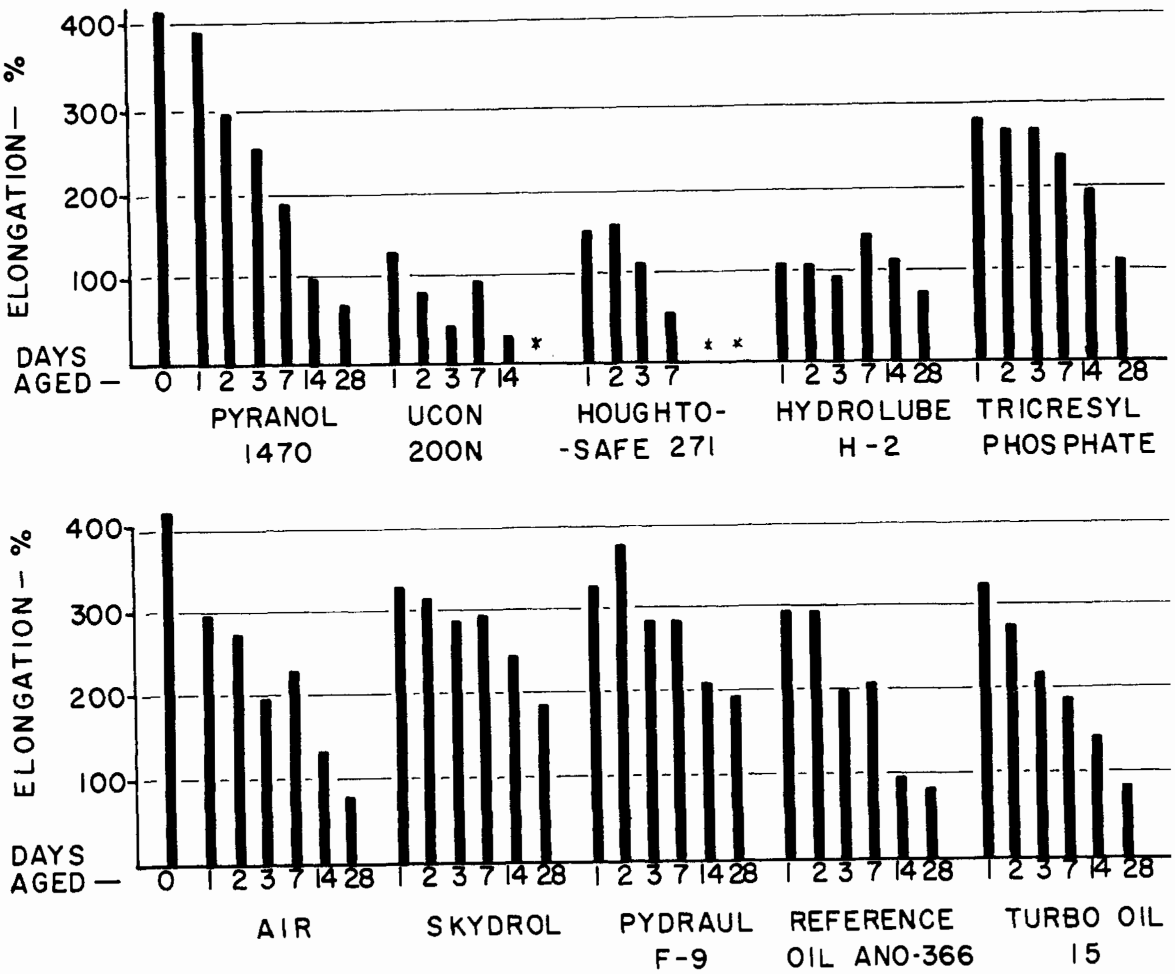

Figure 4. Changes in elongation with aging in air and selected fluids at 212° F.

cure which is obtained with litharge (lead monoxide) is somewhat lower than that which is obtained with lead dioxide. Dibasic lead phosphite and tribasic lead maleate monohydrate can be used to effect a cure but the vulcanizate has somewhat poorer high temperature aging resistance than the magnesium oxide and lead dioxide curing system.

Studies of tensile strength and elongation properties of the oxide cure relative to curing times and temperatures are shown in Figures 1 and 2. It is apparent that the temperature of 330° F. is needed to permit the development, within an economically reasonable curing time, of tensile and elongation properties in a suitable elastomeric range. The long press cure indicated in these graphs is not necessary to develop optimum physical properties. A preliminary press cure of 15 to 30 minutes followed by an air oven postcure at 302° F. will serve to effect the same level of physical properties. Open steam curing has not been very effective in studies with this polymer.

It is not appropriate to hypothesize a vulcanization mechanism at this time. It is apparent from stress relaxation data and high temperature aging studies that cross linking continues while relatively little chain scission occurs under high temperature aging. An extension of the curing curves (Figures 1 and 2) substantiates this cross-linking reaction since the tensile strength increases slowly to a maximum of about 2,000 pounds/square inch and the elongation decreases until a hard, resinous material is formed.

Further evaluation of polyamine curing systems is recorded in Table IV. Physical properties inferior to those of the recommended oxide system were obtained at the level of 3.0 parts of amine.

A GMF and red lead oxide combination proved to be less satisfactory than the oxide cure because of higher original hardness. (GMF is para-quinonedioxime, Naugatuck Chemical Div., U. S. Rubber Co.). Benzoyl peroxide and sodium metasilicate were unsatisfactory.

PHYSICAL PROPERTIES OF OXIDE CURE

Typical original physical properties of Vyram polyacrylic elastomer (recommended oxide cure) are given in Table V. The balance of elongation and ultimate tensile strength values fall within target requirements. Hardness is slightly high and probably results from the high loading by both fillers and metallic oxides. The study of acrylate curing systems in Table II indicates that reduction of the curative loading does improve this property.

Compression Set. The 75 to 85% compression set is considerably higher than the maximum standard previously defined. These results indicate that the oxide cure is not the most advantageous one for satisfactory compression set. Other curing systems outlined in Table II indicate avenues of approach to improve this property.

Aging. The retention of original physical properties upon accelerated heat aging indicates the service life of an elastomer. This matter is of particular importance in hydraulic packing operations, where high temperatures often are maintained. Figures 3, 4, and 5 present changes in the tensile strength, elongation, and hardness properties of the oxide-cured elastomer at 212° F. in air and selected commercial functional fluids. These fluids were picked to cover the types of larger commercial interest, as follows:

TABLE V. OXIDE CURE, TYPICAL ORIGINAL PHYSICAL PROPERTIES[a]

Ultimate tensile strength, lb./sq. inch	1250
Elongation, %	300
Hardness, Shore A	75
Compression set, 25% deflection, 70 hours at 212° F.	75-85% of deflection
Tear, lb./inch	178
Low temperature brittleness	
Pass	+ 14° F. (-10° C.)
Fail	+ 5° F. (-15° C.)
Gehman low temperature torsion test	
T_{10}	36° F.
T_{100}	25° F.
Ozone resistance	Outstanding. No cracks after 1000 hours at 25 p.p.h.m. ozone in static and dynamic tests.
Electrical resistivity	0.0002×10^{13} ohm-cm.

[a] Cured 60 minutes at 330° F.

Solvent	Immersion Conditions		Volume Increase, %		Change in Hardness, Points		% Change			
							Tensile		Elongation	
	Time, days	Temp., ° C.	From	To	From	To	From	To	From	To
Alcohols										
Benzyl alcohol	3	RT	125	130	-30	-40	-85	-95	-65	-75
Cyclohexanol	28	RT	0		- 5	+ 5	+15	+25	-10	-20
	7	100	25	30	+ 5	+10	-10	-20	-55	-65
Dodecyl alcohol	28	RT	0		- 5	+ 5	+20	+30	0	-10
	7	100	5	10	- 5	-10	0	+10	-45	-55
Ethanol	28	RT	5	10	- 5	-15	-10	-20	-15	-25
Isobutanol	28	RT	0	5	- 5	+ 5	0	+10	- 5	-15
Methanol	28	RT	25	30	-15	-20	-45	-55	-15	-25
Tetrahydrofurfuryl alcohol	7	RT	115	125	-40	-50	-85	-95	-65	-75
Aldehydes										
Benzaldehyde	3	RT	350	400	-55	-65	-90	100	-75	-85
Isobutyraldehyde	28	RT	120	130	0	-20	-55	-65	-50	-60
Amines										
Cyclohexylamine	28	RT	20	30	-15	-25	-50	-60	0	+10
tert-Butylamine	28	RT	15	20	- 5	-15	-25	-35	- 5	+10
Di-2-ethylhexylamine	28	RT	0		0	+ 5	+20	+30	0	-10
	7	100	0	5	+ 5	+10	+30	+40	-35	-45
Monoethanolamine	7	RT	10	20	- 5	-15	- 5	-15	-15	-25
	3	100			Sample disintegrated in solvent					
Morpholine	3	RT	300	350	-65	-75	-90	100	-75	-85
Piperidine	28	RT	25	35	-20	-30	-50	-60	-60	-70
Triethanolamine	28	RT	0	5	+ 5	+10	-40	-50	-25	-40
Esters										
Butyl acetate	28	RT	15	20	- 5	-10	-10	-20	-20	-40
Dioctyl adipate		70	0		+10	+15	+15	+25	-25	-35
Dioctyl phthalate	28	RT	0		0	+ 5	+10	+20	-10	-20
	7	100	0		+ 5	+10	+40	+50	-30	-40
Dioctyl sebacate	3	100	0	-5	+10	+15	+20	+30	-25	-35
Ethyl acetate	28	RT	35	40	-15	-25	-55	-65	-50	-60
Ethyl acetoacetate	3	RT	325	375	-55	-65	Too soft to measure			
Ethyl benzoate	28	RT	20	25	-10	-20	-40	-50	-30	-40
	7	100	30	35	-20	-25	-45	-55	-35	-45
Ethyl chloroacetate	3	RT	140	160	-25	-35	-85	-95	-70	-80
Ethyl formate	3	RT	140	160	-45	-55	-90	-100	-55	-65

TABLE VI. IMMERSION DATA ON VYRAM POLYACRYLIC ELASTOMER IN VARIOUS SOLVENTS (Contd.)

	Immersion Conditions		Volume Increase, %		Change in Hardness, Points		% Change			
							Tensile		Elongation	
Solvents	Time, days	Temp. °C	From	To	From	To	From	To	From	To
Ethers										
Anisole	28	RT	55	60	-20	-25	-60	-70	-50	-60
	7	100	45	50	-15	-20	-45	-55	-50	-60
Anethole	28	RT	15	20	-10	-15	-20	-30	-25	-35
	7	100	35	40	-20	-25	-65	-75	-60	-70
Butyl Cellosolve	28	RT	5	10	0	-10	- 5	-15	0	-15
Ethyl ether	28	RT	10	15	-10	-15	-15	-25	-10	-20
Isopropyl ether	28	RT	0		0	- 5	+ 5	+15	0	-10
Methyl Cellosolve	3	RT	135	145	-30	-40	-80	-90	-65	-75
Glycols										
1,4-Butanediol	28	RT	0		0	+ 5	+20	+30	0	- 5
	7	100	10	15	0	+ 5	+ 5	+15	-50	-60
Diethylene glycol	28	RT	0	5	0	- 5	-10	+10	0	- 5
	3	100	60	65	-25	-30	-65	-70	-55	-60
Ethylene glycol	28	RT	0	5	0	- 5	-10	+10	0	- 5
	3	100	275	350	-55	-65	Too soft to measure			
Glycerine	28	RT	0		+ 5	+10	+30	+40	-10	-20
	7	100	5	10	+20	+25	Brittle		Brittle	
Hydrocarbons										
Benzene	28	RT	30	40	-15	-20	-45	-50	-35	-45
Cyclohexane	28	RT	0	10	0	+ 5	+10	+20	0	-10
Cyclohexene	28	RT	5	10	0	- 5	-30	-50	-55	-60
Hexane	28	RT	0	10	0	+ 5	0	- 5	-20	-40
Iso-octane toluene, 70/30	3	RT	0	5	- 5	-10	+15	+25	-15	-25
Isopropyl benzene	28	RT	15	20	0	-10	-25	-35	-30	-40
	7	100	20	25	+ 5	+15	-65	-75	-85	-95
Toluene	28	RT	15	20	0	-10	-25	-35	-25	-35
Xylene	28	RT	10	15	0	-10	0	-10	-15	-25
Ketones										
Acetone	3	RT	150	200	-20	-30	-75	-80	-55	-65
Cyclohexanone	3	RT	200	250	-55	-65	-90	-100	-75	-85
Mesityl oxide	28	RT	40	50	-15	-20	-60	-70	-55	-60
Methyl ethyl ketone	3	RT	85	90	-20	-25	-75	-85	-65	-75
Methyl isobutyl ketone	28	RT	25	30	- 5	-10	-25	-35	-35	-45
Oils										
ASTM oil No. 1	3	100	0	-5	+ 5	+10	+20	+30	-10	-20
ASTM oil No. 3	3	100	0		0	+ 5	+25	+35	-15	-25
Butter	3	70	0	5	Omitted		Omitted		Omitted	
Cottonseed oil	28	RT	0		- 5	+ 5	0	+10	0	-10
	7	100	0	5	+10	+15	- 5	-15	-65	-75
Olive oil	28	RT	0		- 5	+ 5	0	+20	0	-20
	7	100	5	10	+ 5	+10	0	+10	-40	-50
Reference oil, AN-O-366	3	100	- 5	+5	- 5	+ 5	+30	+40	-25	-35
Substituted hydrocarbons										
n-Butyl chloride	28	RT	10	20	- 5	-10	-10	-15	-20	-30
Carbon tetrachloride	28	RT	5	10	- 5	+ 5	+10	+15	-10	-20
0-Dichlorobenzene	3	RT	10	15	Omitted		Omitted		Omitted	
Ethylene dichloride	3	RT	175	225	-25	-30	-75	-85	-65	-75
Methylene chloride	3	RT	200		Omitted		Omitted		Omitted	
2-Nitrobenzene	3	RT	200	250	-55	-65	-85	-95	-75	-85
2-Nitropropane	3	RT	200	250	-55	-65	-85	-95	-65	-75
Trichloropropane	3	RT	225	275	-55	-65	-90	-100	-80	-90
Tetrachloroethylene	3	RT	0	5	Omitted		Omitted		Omitted	
Functional Fluids										
Arochlor 1242	3	100	5	10	0	- 5	+10	+20	-25	-35
Arochlor 1248	3	100	5	10	0	+ 5	+10	+20	-20	-30
Arochlor 1254	3	100	5	10	0	+ 5	+15	+25	-20	-30
Pydraul F-9	3	100	5	10	0	+ 5	0	+10	- 5	-15
Skydrol	3	100	10	15	- 5	-15	+ 5	+20	-25	-35
Skydrol 500	3	100	25	30	-10	-15	-50	-60	-30	-40
Turbo oil 15	3	100	0		+10	+15	+20	+40	-25	-35
	3	150	0	5	+10	+15	+20	+30	-75	-85
Miscellaneous materials										
Carbon bisulfide	3	RT	0	5	0	- 5	-20	-30	-25	-35
Dimethylformamide	3	RT	350	400			Too soft to measure			
Dioxane	28	RT	85	95	-30	-35	-75	-85	-55	-65
Glacial acetic acid	3	RT	100	150			Too soft to measure			
Phenol	3	100					Sample partially disintegrated			
Sodium hydroxide, 10%	3	RT					Too soft to measure			
Sulfuric acid, 10%	7	RT	40	50	0	- 5	-40	-50	0	-10
	28	RT	95	105	-35	-40	-75	-85	-15	-25
Water	3	70	25	30	0	- 5	-25	-35	-25	-35

	Company
Petroleum hydrocarbons	
Reference Oil AN-0-366	Navco Inc., Texaco (No. 2 hydraulic fluid)
Diester	
Turbo Oil -15	Standard Oil of New Jersey
Chlorinated hydrocarbon	
Pyranol 1470	General Electric
Phosphate esters	
Skydrol	Monsanto Chemical
Pydraul F-9	Monsanto Chemical
Tricresyl phosphate	
Glycol based fluids	
UCON 200 N	Carbide & Carbon Chemicals
Houghtosafe 271	E. F. Houghton
Hydrolube H-2	R.M. Hollingshead Corp.

Continued post vulcanization cross linking was observed for Vyram in air and certain of the fluids, as evidenced by increase in tensile strength. In these cases the tensile values reached a plateau after aging for 3 days. Decreases in elongation were observed in all cases, usually reaching a lower plateau in the range of 50 to 200%. Changes in hardness values were erratic. These data would indicate that the oxide-cured elastomer would be satisfactory for applications at 212° F. Other aging studies indicate that 250° F. is a safe temperature limit for the use of this vulcanizate. Cross linking to a brittle state was observed after 48 hours at 300° F.

A variety of conventional and unconventional approaches to stabilize the oxide-cured polymer against thermal cross linking thus far have been unrewarding.

Solvent Resistance. Data are presented in Table VI which show a broad evaluation of the swelling properties of Vyram polyacrylic elastomer in various solvents and fluids. Changes in tensile strength, elongation, and hardness also are recorded. Those swelling data given in Table VII for 28-day periods at room temperature were collected to classify the solvents according to their swelling effects. These data indicate the resistance of the elastomer at room temperature to an unusually wide variety of fluids, notably aliphatic and aromatic hydrocarbons, diesters, phosphate esters, ethers, and certain glycols, amines, alcohols, and miscellaneous fluids. Water resistance is borderline; this probably can be attributed to the elastomers's high solubility parameter.

The selected commercial functional fluids mentioned were utilized for aged volume swelling tests. Figure 6 presents the volume swelling changes in air and fluids over a 4-week period at 212° F. The elastomer exhibited excellent resistance to swelling by the petroleum hydrocarbon, chlorinated hydrocarbon, diester, and one phosphate ester (Pydraul F-9). Its resistance to swelling by tricresyl phosphate and Skydrol hydraulic fluid was within acceptable limits over this extended period. Poor swelling resistance was encountered with the glycol-based fluids. The temperature of 212° F. employed in this series of tests is above the 130° to 160° F. recommended operating temperatures for Skydrol and the glycol-based fluids, but 212° F. may be encountered in some applications.

TABLE VII. SWELLING CHARACTERISTICS OF VYRAM POLYACRYLIC ELASTOMER IN VARIOUS SOLVENTS IMMERSED 28 DAYS AT ROOM TEMPERATURE

Volume Swelling, %

0 Excellent	10 Good	25 Fair	75 Poor	150 Very Poor
Cyclohexanol				
Ethanol				Benzaldehyde
		Methanol		
			Isobutyraldehyde	
		Cyclohexylamine		
				Morpholine
		Piperidine		
Triethanolamine				
Dioctyl adipate				
Dioctyl phthalate				
Dioctyl sebacate				
	Butyl Cellosolve	Anisole		
Diethylene glycol			Methyl Cellosolve	
Ethylene glycol				
Glycerine				
Cyclohexane		Benzene		
Hexane				
Iso-octane/Toluene, 70/30				
	Toluene			Acetone
ASTM Oil #1			Methyl ethyl ketone	
ASTM Oil #3				
Reference Oil An-0-366				
	Carbon tetrachloride			
	o-Dichlorobenzene			Nitrobenzene
				Trichloropropane
Tetrachloroethylene				
	Arochlor 1248			
Pydraul F-9				
	Skydrol	Skydrol 500		
Turbo Oil 15				
Carbon bisulfide				Dimethyl formamide
			Dioxane	
				Glacial acetic acid
		Water		Phenol

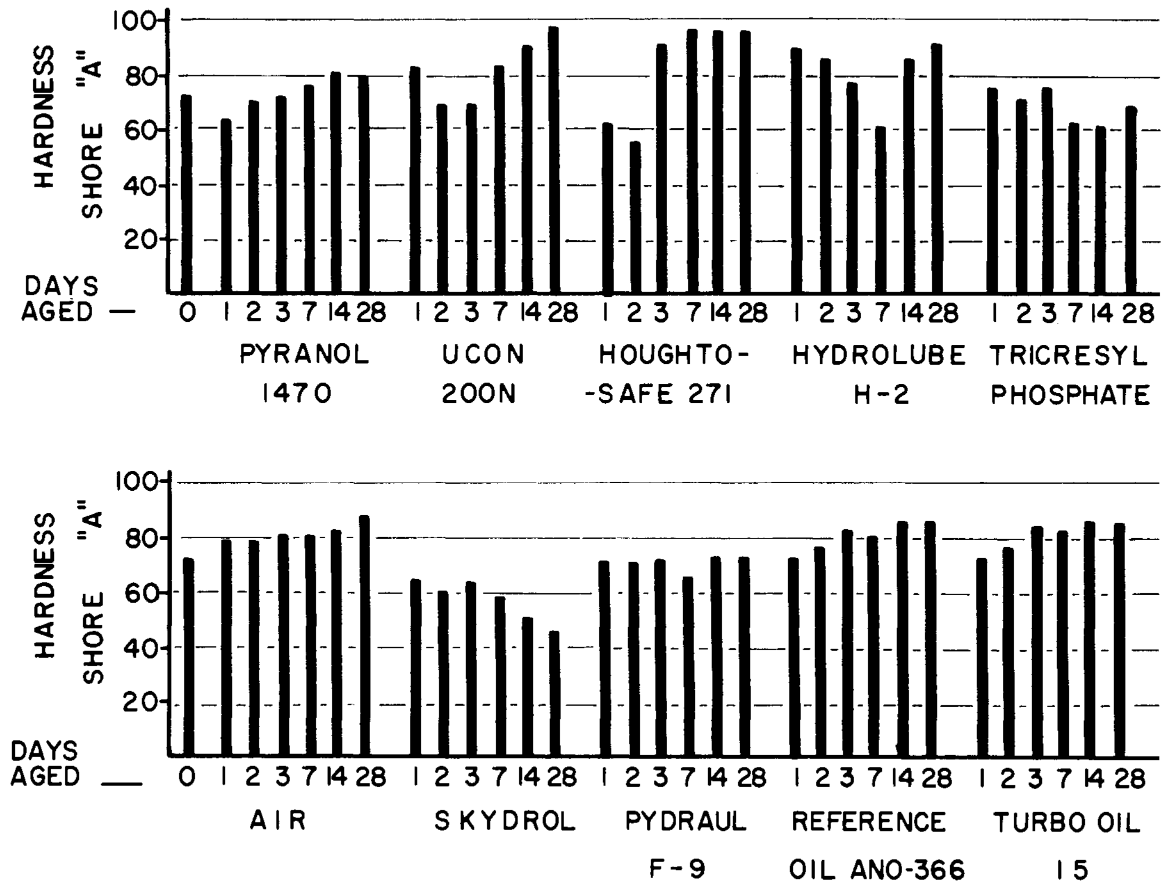

Figure 5. Changes in hardness with aging in air and selected fluids at 212° F.

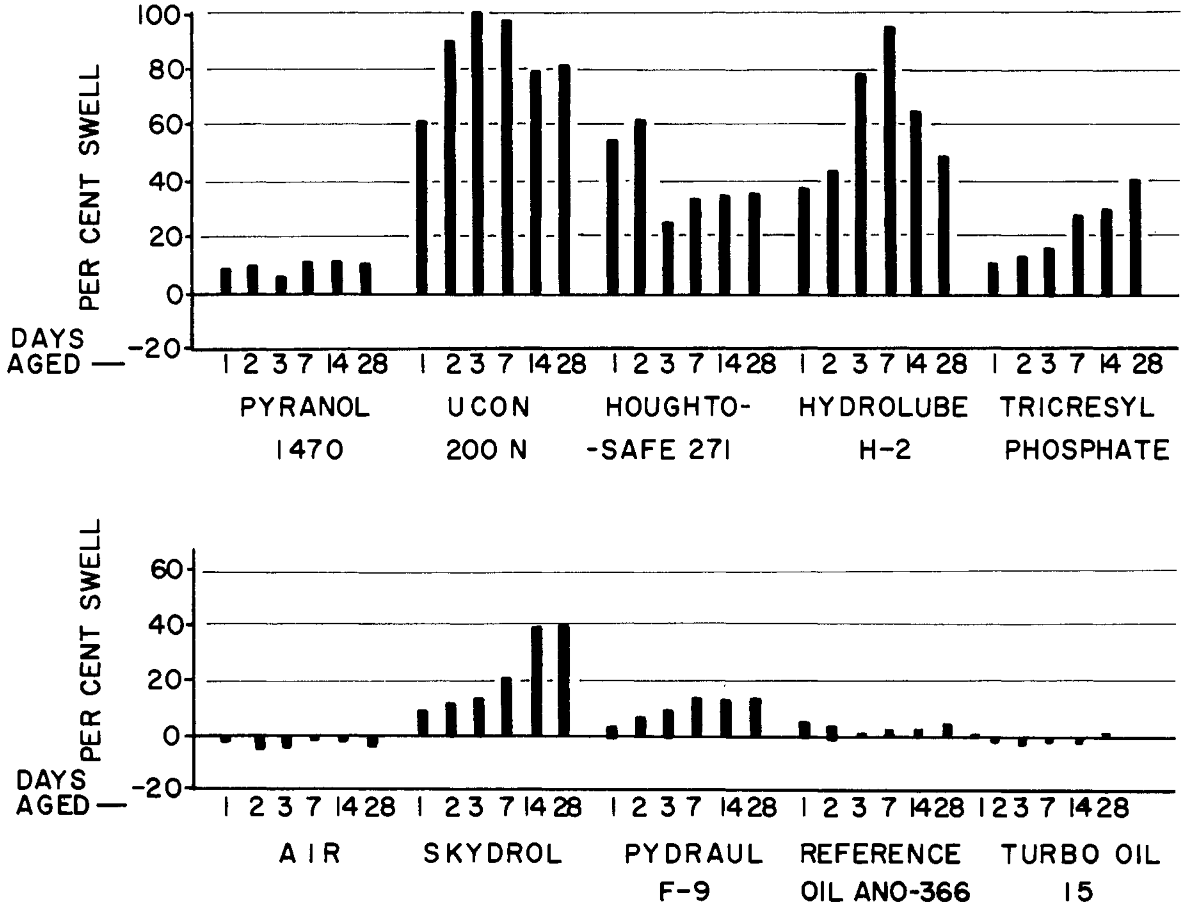

Figure 6. Volume changes in air and fluids at 212° F.

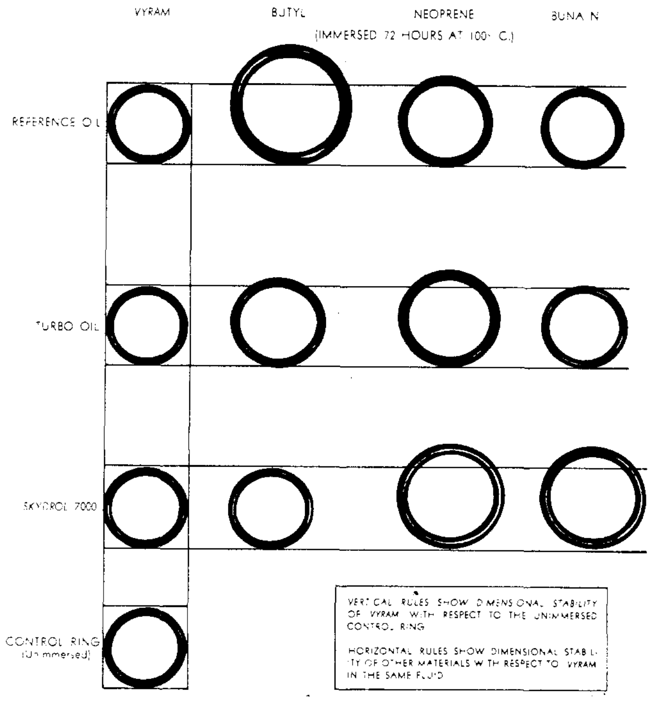

Figure 7. Swell comparisons of Vyram, butyl rubber, neoprene, and nitrile rubber O-rings after 72 hours at 212° F. in reference oil, AN-O-366, Turbo Oil-15, and Skydrol hydraulic fluid

In still another study, O-rings compounded from Vyram, butyl rubber, Neoprene, and nitrile rubber were subjected to immersion for 72 hours at 212° F. in Reference Oil AN-0-366, Turbo Oil-15, and Skydrol 7000 hydraulic fluid. The comparisons of the O-rings at the completion of the test (Figure 7) strikingly show that Vyram was the only one which retained substantially its original dimensions in all three types of fluids.

In a field test, a nacelle-door gasket was produced for evaluation on a commercial airplane. In this evaluation the part was subjected to drippings from a hydraulic system containing Skydrol hydraulic fluid and it was also contacted by gasoline, water, and lubricating oils. After 1600 hours of service the gasket was unaffected by the fluids and retained substantially its original dimensions. Standard synthetic elastomeric parts had been known to deteriorate in 100 hours in this test.

The degree of swelling of a polymer in a fluid has been related by Gee (4) and others to the relative values of a fundamental constant of the materials which is called the solubility parameter or the cohesive energy density. This constant is calculated by taking the square root of the quotient of the heat of vaporization and the molal volume. For polymers the solubility parameter is estimated by measuring the solubility or degree of swelling in a spectrum of solvents covering the range of (cohesive energy density) values. The unusual solvent resistance of Vyram polyacrylic elastomer can be attributed to its high solubility parameter of 10.2. This value is above the constant for most functional fluids. This fact, in part, accounts for the excellent solvent resistance of Vyram polyacrylic elastomer.

Electrical Resistivity. The low electrical resistivity of the oxide cure is not surprising in view of the presence of conductive black in the recipe. This is not a conclusive representation of the electrical properties of the elastomer which may be upgraded by the development of other systems of fillers and vulcanizing agents.

Low-Temperature Properties. The elastomer exhibits the low-temperature brittleness range characteristic of acrylate elastomers. However, this deficiency can limit its utility for meeting military specifications. The spectrum of acrylate curing systems in Table II indicates no promise of improvement through the choice of a curing system. Plasticization was a logical approach, but initial results of the evaluation of various commercial plasticizers were unrewarding, as evidenced by drastic drops in properties of the elastomer without significant improvement of low-temperature properties.

PROCESSING METHODS

Various fabricators have made finished parts by conventional molding and extrusion techniques. Dispersions of the elastomer have been prepared in solvents such as ethylene dichloride and acetone to permit coating application. No information is available on the calendering properties of the elastomer.

END USES

The unusual solvent resistant properties of Vyram polyacrylic elastomer suggest its applicability for oil rings, hoses, seals, O-rings, chevrons, gaskets, coated rollers, and coated fabrics. The product already has shown considerable promise in a number of these applications. Studies now in progress are expected to result in improvement in hardness, compression set, aging, and electrical properties.

SUMMARY

A new elastomer in the class of polyacrylic etheresters has exhibited outstanding resistance to swelling by a wide variety of solvents and functional fluids, excluding glycol-based fluids. A vulcanizate has been developed to yield satisfactory service performance in air and fluids in the temperature range of 10° to 250° F. A number of end uses are suggested to take advantage of the present properties of the elastomer.

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