

Noncorrosive Nitrile Elastomers*

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Synopsis

The corrosion of steel by nitrile elastomer oil seals prompted a laboratory study of the corrosivity of numerous compounding ingredients and nitrile polymers. Groups of materials studied in this investigation were plasticizers, antioxidants, black fillers, nonblack fillers, curing systems, and base polymers. A corrosion test procedure utilizing a bench-type corrosion chamber was developed, and a corrosion rating system was established. All materials were rated according to their corrosivity under conditions of 100% R. H., and 100°F. for 96 hr. From these data it was possible to formulate several noncorrosive seal compounds without the use of corrosion inhibitors.

INTRODUCTION

Rubber-induced corrosion is not a new problem. It has been reported by Pickett¹ and Perry et al.² Elastomers sandwiched between steel plates are known to produce corrosion.³ Symons⁴ has recently reported corrosion of steel shafts by lip-type seals. Litharge has been used successfully as a corrosion inhibitor in seal compounds.⁵ However, the use of litharge results in a considerable sacrifice in compression set.

Laboratory studies indicated that nitrile seal materials can cause corrosion of steel under conditions of high humidity. It was the primary objective of this investigation to formulate a noncorrosive elastomer for oil seals. To achieve this goal, it was first necessary to establish a corrosion test procedure and to develop a bench-type humidity chamber.

EXPERIMENTAL

Sample Preparation and Test Procedure

The elastomeric compounds were milled following normal procedures with special care to prevent contamination. The compounds were molded into ASTM slabs in chrome-plated molds in the absence of a mold release, since some mold releases were found to cause corrosion. The first slab was discarded and the second was retained for testing. A $1 \times \frac{1}{4}$ in. piece was die-cut from each slab, dipped in ethanol, and air-dried 1 hr. before assembling in the test fixture (Fig. 1). Polymer gums were treated in the

* Paper presented before the Division of Rubber Chemistry, American Chemical Society, Cleveland, Ohio, October 17-19, 1962.

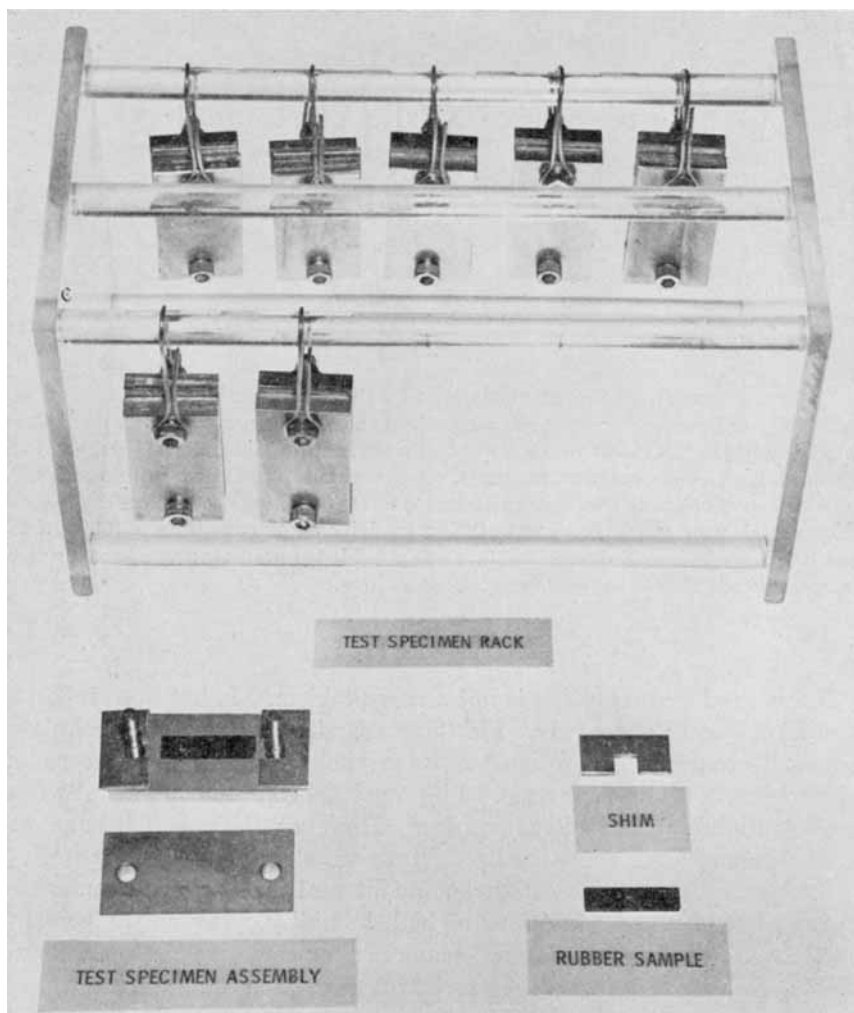


Figure 1.

same manner, except that it was necessary to cool them in the press before removal from the mold. Metal plates, $1 \times 2 \times \frac{1}{4}$ in., of SAE 1020 steel were cadmium-plated. The cadmium was removed from one side of the steel plate by grinding to a 10μ in. finish. The steel specimens were first rinsed in toluene, followed by a methyl ethyl ketone rinse to remove all contamination. The elastomer was placed between the ground surfaces of two plates, bolted, and through the use of shims, the sample was compressed 0.005–0.009 in. The assembled sample was hung on an acrylic plastic rack (Fig. 1) and was heated to 100°F . for 1 hr. before being placed in the humidity test chamber. The test conditions used throughout this investigation were: 100% R. H. and 100°F . for 96 hr. At the termination of the test, the sample was removed from the humidity chamber and dis-

assembled. The plates, free of the elastomer, were dipped in naphtha and rubber with a soft cloth to remove any adhering elastomer. The plates were polished with crocus cloth to remove any stains and were rated by visual observation.

Bench-Type Humidity Chamber

The equipment used in this test included a standard laboratory vacuum desiccator with a 10 in. i.d. and an air circulating oven capable of housing the desiccator and maintaining a temperature of $100 \pm 2^\circ\text{F}$. A relative humidity of 100% was produced by placing 500–1000 ml. of water in the bottom of the desiccator and placing the desiccator in the oven at 100°F . (Fig. 2).

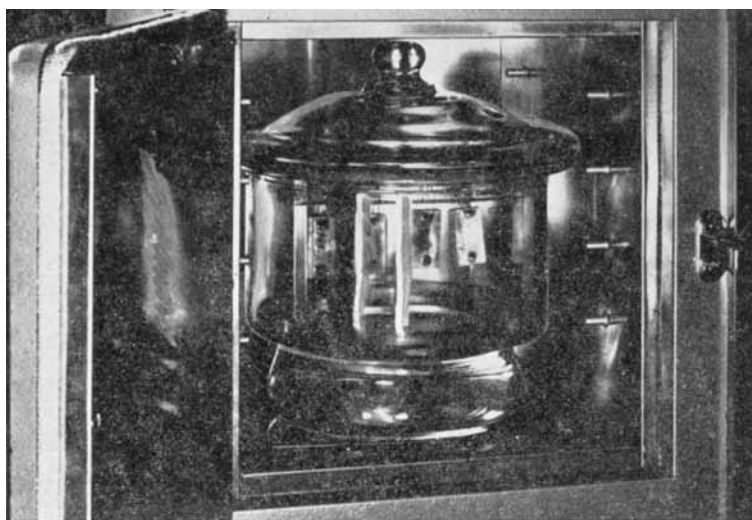


Figure 2.

In the early phases of the program, corrosion tests were conducted in a walk-in humidity room in which the humidity was controlled by steam. Good correlation of the corrosion produced in the desiccator vs. the humidity room was obtained. All corrosion data reported in this paper were obtained with the bench-type humidity chamber.

Corrosion Rating System

A corrosion rating scale was developed by taking double-sized photographs of all the corrosion samples and sorting them according to the degree of corrosion, from no corrosion to severe corrosion. The corrosion rating photograph is shown in Figure 3. The rating scale varies from 0 (no corrosion) to 5 (severe corrosion). A corrosion rating of 1 or less is acceptable. For each corrosion rating, three photographs represent different types of corrosion with the same rating. This was done to illustrate

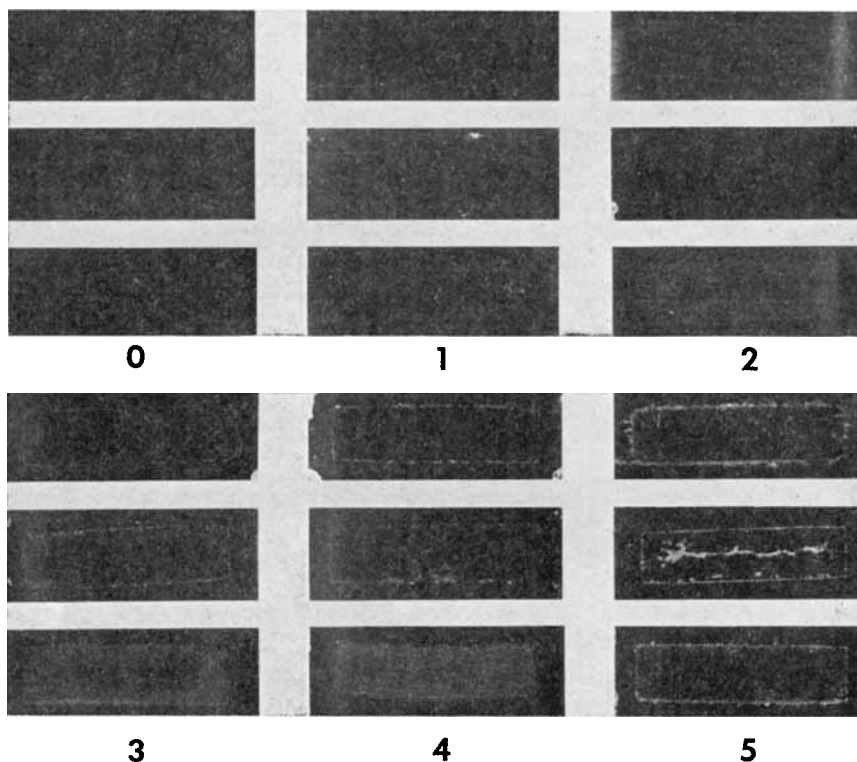


Fig. 3. GMR corrosion rating system.

the different kinds of corrosion that can be produced with the same severity. The top photo in each rating, except 0, exhibits corrosion around the edge of the rubber sample. The middle photo shows edge corrosion plus some internal corrosion. The bottom photo exhibits over-all general corrosion. The laboratory practice of elastomer corrosion rating is performed by a visual comparison of the corroded steel plates with the corrosion rating photograph.

RESULTS AND DISCUSSION

Noncorrosive Seal Compounds

As the best approach to formulating a noncorrosive seal compound, it was decided to use a selected combination of the least corrosive polymer and compounding ingredients. Therefore comparative corrosion tests were conducted on polymers without additives and also on compounding ingredients. Each compounding ingredient was evaluated by combining with the polymer and other essential ingredients necessary to produce a cured compound. Classes of compounding ingredients investigated were: fillers, antioxidants, plasticizers, and curing systems.

Polymers

Several nitrile polymers were tested for corrosivity. Three polymers of those found to be noncorrosive were selected for compounding studies. They are: Hycar 1042X100, Chemigum N6B, and Paracril BLT, all acrylonitrile-butadiene copolymers containing 30–34% acrylonitrile.

TABLE I
Corrosion by Carbon-Black Fillers*

Filler	Type	Rating
Control, no rubber	—	0
Cabot Regal 300	ISAF oil	0-1
Cabot Regal SRF	SRF oil	0-1
Sterling SO	FEF oil	1
Graphite SF	Flake	0-1
Graphite 518	Powder	1
Cabot Regal 600	ISAF oil	2
Vulcan C	CF oil	4
Sterling V	GPF oil	3
Sterling FT	FT gas	3
Spheron 9	EPC gas	3
Vulcan 3	HAF oil	3
Sterling MT	MT gas	3
Sterling L	HMF gas	5
Vulcan 6	ISAF oil	5
Sterling S	SRF gas	4
Control-Cured Paracril BJ		5

* Carbon-black formulation: Paracril BLT, 100 parts; Protox 166-zinc oxide, 2.5 parts; Spider sulfur 1.5 parts; Tuex 0.2 part; filler, 75 parts; cure: press 80 min. at 300°F.

TABLE II
Corrosion by Nonblack Fillers

Filler	Type	Rating
Control, no rubber	—	0
Hydrite R	Clay, calcined	3
Glomax HE	Clay, calcined	2
Suprex	Clay, dry-ground	2
Glomax PVR	Clay, calcined	2
REM 7	Clay, water-washed, surface-modified	2
Glomax LL	Clay, calcined	4
Control, cured Paracril BJ	—	4
Atomite	CaCO ₃ , wet-ground	4
Keystone	CaCO ₃ , dry-ground	4
Calcene NC	CaCO ₃ , precipitated	5
Hi Sil 233	Silicon dioxide	5+
Silene EF	Calcium silicate	5+

Carbon-Black Fillers and Graphite

Thirteen carbon-black fillers and two graphites were evaluated to determine what part each plays in the corrosion of steel when used as a compounding ingredient. The formulation and the corrosion test results are shown in Table I. The carbon blacks were obtained from the Cabot Corporation. The two rubber grade graphites used were obtained from Asbury Graphite Mills Inc. Compounds with Regal 300, Regal SRF, and Graphite SF exhibited negligible corrosion, while those containing Sterling SO and

TABLE III
Corrosion by Plasticizers*

Plasticizer	Class	Rating
Control, no rubber	—	0
Dibenzyl sebacate	Ester	0
Dibutyl sebacate	Ester	0-1
Control, rubber, no plasticizer	—	1
Paraplex G-25	Polymeric	1
Cumar W2- ¹ / ₂	Resin	2
Plasticizer SC	Ester	2
Dibutyl phthalate	Ester	2
Diocetyl phthalate	Ester	3
Cumar P-25	Resin	3
TP 90B	Polymeric	3
KP 140	Ester	3
Hycar 1312	Polymeric	3
Control, cured Paracril BJ	—	5

* Plasticizer formulation: Paracril BLT, 100 parts; Protox 166-zinc oxide, 2.5 parts; Spider sulfur, 1.5 parts; Cabot Regal SRF, 60 parts; Tuex, 0.2 part; plasticizer, 20 parts; cure: press 80 mins. at 300°F.

TABLE IV
Corrosion by Antioxidants*

Antioxidant	Class	Rating
Control, no rubber	—	0
AgeRite White	Amine	0-1
AgeRite Hipar	Amine	2
AgeRite Alba	Ether	2
Antioxidant 2246	Phenol	2
Ozo 88	Amine	2
Aminox	Amine	2
AgeRite Powder	Amine	2
Control, no antioxidant	—	2
AgeRite Superlite	Phenol	3
AgeRite Resin D	Polymeric	3
Octamine	Amine	3
AgeRite Resin	Amine	4
Control, cured Paracril BJ	—	5

* Antioxidant formulation: Paracril BLT, 100 parts; Protox 166-zinc oxide 2.5 parts; Spider sulfur 1.5 parts; Tuex 0.2 part; antioxidant 5 parts; cure: Press 80 min. at 300°F.

Graphite 518 showed slight corrosion. Previous test results not shown here indicate that polymers compounded according to the formulation in Table I, but without fillers, are corrosive. Since some of these black-filled compounds are less corrosive than the nonfilled compound, these black fillers must either inhibit corrosion or dilute the curing agents so as to make their corrosive effect negligible. Blacks of the same type, e.g., SRF, made by different methods, oil vs. gas, exhibit varying degrees of corrosion.

Nonblack Fillers

Eleven nonblack fillers were evaluated for corrosivity. These include clay, calcium carbonate, silicon dioxide, and calcium silicate. The same

TABLE V
Corrosion by Curing Systems*

Compound	Curing system	Rating
A-1	Spider sulfur, 1.5; Monex, 4.5	0-1
A-2	Spider sulfur, 4.5; Monex, 1.2	1
A-3	Spider sulfur, 4.5; Monex, 0.75; Altax, 4.5	2
A-4	Tuex, 5	0-1
A-5	Spider sulfur, 1.5; Tuex, 3	0-1
A-6	Altax, 2; Tuex, 4	0-1
A-7	Tuex 1; Sulfasan R, 1.5	2
A-8	Tuex, 3; Santocure, 3	1
A-9	Spider sulfur, 0.5; Tuex, 2; Santocure, 1	1
A-10	Spider sulfur, 0.3; Tuex, 1; Altax, 2	1
A-11	Spider sulfur, 0.2; Tuex, 3; Altax, 4.5	1
A-12	Spider sulfur, 1.5; Tuex, 0.25; Altax, 1.5	3
A-13	Spider sulfur, 1.5; Altax, 1.5	3
A-14	Spider sulfur, 1.5; Altax, 1.5; Cumate, 0.2	3
A-15	Spider sulfur, 0.4; Altax, 3; Methyl Zimate, 1.5	2
A-16	Spider sulfur, 1.5; Altax, 1.5; Methyl Zimate, 0.15	2
A-17	Spider sulfur, 0.2; Altax, 2; Ethyl Selenac, 3	3
A-18	Spider sulfur, 1.5; Santocure, 0.75	3
A-19	Altax, 1.5; Ethyl Selenac, 3.5	1
A-20	Spider sulfur, 1.5; Methyl Zimate, 1.5, Captax, 1.5	3
A-21	Spider sulfur, 1.5; Captax, 1.5; DPG, 1.2	4
A-22	Spider sulfur, 0.5; Bismate, 1.5	3
A-23	Spider sulfur, 1.5; Bismate, 0.6	3
A-24	Spider sulfur, 1.5; Ethyl Selenac, 0.75	2
A-25	Tetrone A, 2	2
A-26	Spider sulfur, 0.2; Tetrone A, 1.5	1
A-27	Dicup 40 HAF, 5	1
A-28	Spider sulfur, 1; NOBS #1, 1	1
A-29	Spider sulfur, 1; NOBS Special, 1	1
A-30	Spider sulfur, 1; DIBS accelerator, 1	1
A-31	Control, Paraacril BLT alone	0
A-32	Control, Paraacril BLT, 100; Protox 166, 5; stearic acid, 1	0

* Curing systems formulation: Paraacril BLT, 100 parts; Protox 166-zinc oxide, 5 parts; stearic acid (Baker), 1 part; curing system variable, see above; cure: press 20 min. at 310°F. except A-31 and A-32; A-31 and A-32 formed 10 min. at 300°F. and cooled to room temperature for 20 min.

TABLE VI
Elastomer Seal Formulations^a

Ingredients	Compound number															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Protax 166	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Spider sulfur	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Aminox	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
AgeRite White	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Stearic acid (Baker)	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
Regal SRF Black	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65
Sterling SO Black	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Dibenzyl sebacate	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Paraplex G-25	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Tuex	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Monex	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Altax	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2

^a Cure: press 20 min. at 310°F.

formulation and cure used in the black-filler study was followed. The test results are listed in Table II. The clays exhibit the least corrosion, being only fair. The calcium carbonates show heavy corrosion, while silicon dioxide and calcium silicate are very corrosive.

Plasticizers

Several types of plasticizers were evaluated; namely, ester, polymeric, and resin. These plasticizers were chosen because they are commonly used in nitrile formulations. The formulation and the corrosion test results are listed in Table III. The sebacates exhibited no corrosion to very slight corrosion. These are the only two plasticizers tested which showed less corrosion than the control which had no plasticizer. Polymeric Paraplex G-25 showed corrosion equivalent to that of the control.

Antioxidants

Representative antioxidants (e.g., amine, phenol, ether, and polymeric) commonly used in nitrile compounding were evaluated. The formulation and corrosion test results are listed in Table IV. None of the antioxidants were successful in completely inhibiting corrosion. However, several were able to improve corrosion resistance. The control sample which had no antioxidant is number 8 in order of corrosion. All of those above this control exhibited less corrosion than the control even though most have the same rating number. AgeRite White proved to be the least corrosive. No one class of antioxidants showed superior corrosion resistance. Variations in degree of corrosion within the classes are widespread.

TABLE VII
Corrosion Test Results of Seal Compounds^a

Test 1		Test 2		Test 3		Test 4	
Compound	Rating	Compound	Rating	Compound	Rating	Compound	Rating
NR Control	0	NR Control	0	NR Control	0	NR Control	0
H-1	0-1	H-5	0-1	H-9	0	H-13	0
H-2	0	H-6	0	H-10	0	H-14	0
H-3	0	H-7	0-1	H-11	0	H-15	0
H-4	0-1	H-8	0	H-12	0	H-16	0
B-1	2	B-5	3	B-9	2	B-13	3
B-2	1	B-6	4	B-10	1	B-14	2
B-3	2	B-7	2	B-11	2	B-15	1
B-4	2	B-8	2	B-12	3	B-16	2
N-1	4	N-5	4	N-9	4	N-13	2
N-2	4	N-6	4	N-10	4	N-14	2
N-3	4	N-7	4	N-11	4	N-15	3
N-4	3	N-8	4	N-12	4	N-16	3
BJ Control	5	BJ Control	5	BJ Control	4	BJ Control	5

^a NR = no rubber; H = Hycar 1042×100; B = Paracril BLT; N = Chemigum N6B; BJ = Paracril BJ cured with minimum curatives.

TABLE VIII
 Properties of Noncorrosive Seal Compounds

Physical properties	H-2	H-3	H-6	H-8	H-9	H-10	H-11	H-12	H-13	H-14	H-15	H-16
Tensile, psi	2725	2455	3040	2755	2080	2475	2130	2520	2160	2565	2105	2305
Elongation, %	235	305	290	275	505	470	525	475	505	490	500	425
Durometer, Shore A-2	76	73	76	75	69	70	69	70	68	69	69	70
Tear, lb./in.	310	260	245	250	350	330	410	350	370	385	345	345
Modulus, psi												
100% elongation	1015	800	985	1015	365	445	385	445	365	405	380	480
200% elongation	2390	1815	2315	2320	910	1105	905	1115	910	1055	895	1165
300% elongation		2455			1455	1815	1450	1790	1505	1755	1435	1850
400% elongation					1870	2290	1895	2260	1975	2270	1895	2260
500% elongation					2050		2105		2140		2195	
Compression set												
Method B (70 hr. at 250°F.)												
Set, %	25	25	24	27	48	47	44	40	39	40	44	42
Cold test D746												
T _b brittleness, °C.	-37	-32	-39	-38	-36	-39	-34	-39	-36	-36	-34	-37
T _b , °F.	-35	-26	-38	-36	-33	-38	-29	-38	-33	-33	-29	-35

GMR corrosion rate	0-1	0	0	0-1	0	0	0	0	0	0	0	0
Mooney Scorch	14 ² / ₃	11	11 ¹ / ₃	13 ¹ / ₃	21+	21+	21+	21+	21+	21+	11 ¹ / ₃	12
<i>T_c</i>												
Aged properties (70 hr. at 250°F.)												
In ASTM #1												
% change, tensile	-0.6	+11	+5.8	+8.6	+20	+11	+18	+9.3	+18	+10	+21	+14
% change, elongation	-26	-26	-17.2	-18	-32	-27	-41	-36	-22	-25	-20	-21
% change, volume	-3.7	-3.5	-3.1	-3.9	-3.1	-4.0	-3.1	-3.4	-3.3	-4.1	-3.4	-3.5
Points change, duro.	+4	+6	+4	+4	+3	+4	+6	+4	+4	+3	+3	+5
In ASTM #3												
% change, tensile	-5.9	+1.2	-10	0	+11	+0.4	+7.5	+2.2	+12	-1.9	+13	+13
% change, elongation	-23	-20	-28	-16	-23	-28	-23	-22	-19	-25	-11	-9.4
% change, volume	+12	+12	+12	+12	+14	+14	+14	+15	+14	+14	+14	+14
Points change, duro.	-6	-6	-6	-5	-9	-10	-10	-9	-9	-11	-13	-11
Air oven												
% change, tensile	+13	+14	+3.9	+12	+20	+14	+16	+8.5	+23	+9.9	+15	+20
% change, elongation	-21	-21	-28	-18	-39	-34	-36	-28	-34	-34	-27	-22
% change, volume	-0.9	-1.0	-0.8	-1.3	-0.9	-1.7	-0.9	-1.0	-1.5	-1.0	-0.9	-0.9
Points change, duro.	+5	+7	+5	+5	+8	+7	+7	+7	+7	+6	+6	+5

Curing Systems

The curing systems investigated in this program consisted of accelerators and/or vulcanizing agents. The zinc oxide–stearic acid combination of accelerator-activators, which was found to be noncorrosive, was not varied in the formulations. The formulations and corrosion test results are shown in Table V. An analysis of the 30 curing systems shows that all of the systems exhibit some degree of corrosion. Four of these systems are recommended as being least corrosive: A-1, A-4, A-5, and A-6.

Seal Compounds

Based on the data reported in this paper, 16 seal compounds have been formulated using the least corrosive materials (See Table VI). Three noncorrosive nitrile polymers have been used in these formulations, so that the total number of seal compounds tested was 48. The compounds were milled in batches of eight and cured the following day. The test conditions were the same as used in the initial phase of the investigation, namely 100% R. H. and 100°F. for 96 hr. Four formulations of each of the three polymers were tested simultaneously with two controls. The controls included a no-rubber control and a cured polymer control. This procedure was chosen so that any variation in test conditions would have an equal effect on the three polymers in their respective formulations and a valid comparison between them could be made. The corrosion results are shown in Table VII. It was necessary to conduct four 96-hr. tests in order to evaluate all 48 compounds. In Table VII, H-1 stands for Hycar 1042×100 polymer used in compound formulation 1, B-1 for Paracril BLT polymer used in compound formulation 1, and N-1 for Chemigum N6B polymer used in compound formulation 1, etc. The test data show that several compounds made with the Hycar polymer exhibit no corrosion. All of the Paracril and Chemigum compounds exhibited some corrosion with ratings varying from 1 to 4.

The noncorrosive compounds made with Hycar 1042×100 were tested to determine their oil seal properties. The test results are listed in Table VIII. All of the compounds exhibit good heat and oil resistance and compression set properties.

CONCLUSIONS

The three objectives of this investigation have been achieved. A corrosion test procedure has been established. A bench-type humidity chamber has been developed and correlated with the humidity room. As a part of the latter development, a corrosion rating system has been established. And finally, several noncorrosive oil seal elastomers have been prepared and their properties determined.

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Résumé

La corrosion de l'acier par des huiles d'élastomères nitriliques a incité une étude de laboratoire sur le pouvoir de corrosion de nombreux ingrédients de composition et de polymères nitriliques. Les groupes de matériaux étudiés dans ce travail étaient des plastifiants, des antioxydants, des produits de charge noirs, des produits de charge noirs, des systèmes de traitement et des polymères de base. On a développé un procédé d'expérimentation utilisant une chambre de corrosion du type à banc et on a établi un système d'évaluation de la corrosion. On a évalué le pouvoir de corrosion de tous ces matériaux sous des conditions de 100% d'humidité relative et à 100°F durant 96 heures. Au départ de ces résultats il a été possible de désigner plusieurs composés de soudure non-corrosifs sans devoir recourir à des inhibiteurs de corrosion.

Zusammenfassung

Die Korrosion von Stahl durch Ölfangringe aus Nitrilelastomeren führte zu einer Laboratoriumsuntersuchung der Korrosionswirkung zahlreicher Mischungszusätze und Nitrilpolymerer. Untersucht wurden folgende Stoffgruppen: Weichmacher, Antioxydantien, Russe und andere Füllstoffe, Vulkanisationssysteme und Polymere. Ein Korrosionstest unter Benützung einer Korrosionskammer vom Banktyp wurde entwickelt und ein Bewertungssystem aufgestellt. Alle Stoffe wurden nach ihrer Korrosionswirkung bei 100% relativer Feuchtigkeit bei 100°F während 96 Stunden eingestuft. Die Ergebnisse ermöglichten die Formulierung einiger nicht-korrozierender Mischungen ohne Verwendung von Korrosionsinhibitoren.

Received January 16, 1963