

CORROSION INHIBITING RUBBER SEALS

B. A. Miksic
Northern Instruments Corp.

W. G. Levans
Garlock, Inc.

Society of Automotive Engineers
International Automotive Engineering
Congress and Exposition
Cobo Hall, Detroit
February 28, - March, 1977
770174

ABSTRACT

A new oil seal rubber compound has been developed with considerably improved GMRP corrosion rating. This was achieved by compounding the basic Hycar 1042 elastomer with compatible corrosion inhibitor, capable of inhibiting the corrosion process on rubber-metal interface. The inhibitor was compounded at 5% by weight level, and was found protective to steel, aluminum, brass and bronze. High degree of protection was achieved under increased temperature and humidity conditions, and promising results obtained in various test fluids including common oils and fuels.

INTRODUCTION

SOME ELASTOMERIC SEAL compounds show a tendency to induce corrosion of metals. The corrosion of metals. The corrosion inducing mechanism is not completely understood, but it is believed that certain compounding ingredients are responsible for the corrosive action.

The problem of corrosion on rubber-metal interface has been especially pronounced in the automotive and aircraft industries. Many failures of seals were caused by the corroding effect of seal material under conditions of high humidity. Extensive research has been conducted to study the effect of the compounding ingredients on corrosion of steel (1). * Many carbon black fillers, antioxidant, plasticizers and curing systems were reported corrosive.

Very little has been done in the past to develop corrosion inhibitors suitable for incorporation in elastomeric seal materials. Investigations on potassium dichromate, litharge, and certain cationic surfactants, show corrosion inhibitors of that type being generally ineffective (2).

GENERAL

The purpose of our investigation was to formulate a corrosion inhibiting system that would inhibit the attack on the metal substrate. To be practically applicable, the inhibiting chemicals would have to be added at the compounding stage with the rest of compounding ingredients and would have to be of zero or low toxicity and pollution.

In spite of the simplicity of this idea, its realization proved to be a rather complex task. It is widely known in rubber chemistry and technology that introduction of non-compatible substances can adversely affect some of elastomer's distinctive mechanical and chemical properties. The goal of our investigation was to keep original properties unchanged when transforming an elastomer from a corrosion initiating to a corrosion inhibiting material.

In order to choose the right corrosion inhibitor, we had to ascertain that a prospective compound had a suitable chemical structure for incorporating in the elastomer, as well as the capability of forming a stable bond with the metal surface. A serious consideration has been given to compatibility with existing production processes, the main factors being the absence of any deleterious effects on curing kinetics and ease of mixing and dispersing in the host polymer.

Theoretically, miscibility of any compound with the polymer depends upon the magnitude of their heat of mixing:

$$H_{\text{mix}} = V_1 V_2 (\delta_1 - \delta_2)^2 \quad (1)$$

H_{mix} = Heat of mixing per unit volume.

V_1 and V_2 = volume fractions of components.

δ_1 and δ_2 = solubility parameters of the components

In an ideal case the heat of mixing equals zero, which implies that the values of solubility parameters (δ_1 , δ_2) are equal. In our case, it would mean that the corrosion inhibitor is miscible with the base polymer, if its δ_1 value is equal to δ_2 value of the polymer.

$$\delta_1 = \left(\frac{H_u - TR}{M/d} \right)^{1/2} \quad (2)$$

where: H_u = heat of vaporization

R = gas constant

M = molecular weight

d = density

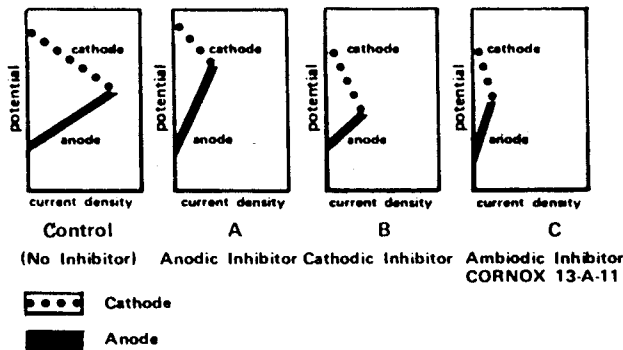


Fig.1 – Electrochemical mechanism of CORNOX inhibitors (schematic polarization diagrams)

___ Based on theoretical considerations, it was possible to develop and laboratory model which proved convenient for predicting the dispersibility of experimental corrosion inhibiting systems.

* Numbers in parentheses designate References at end of paper.

THE MECHANISM

An investigation of the kinetics of electrochemical reactions demonstrated the CORNOX inhibitors* included in this study were “ambiodic” in their behavior. “Ambiodic” means that they are capable of changing the kinetics of both cathodic and anodic electrochemical reactions (Fig. 1).

Strong inhibition of anodic reaction is due to two acceptor-donor adsorption centers, participating in the formation of chemical bonds between the metal and the inhibitor. Adsorption of these compounds changes the energy states of ion atoms of metal on the surface, which is indicated by decrease of electron work function. The increase of contact potential difference by more than 0.3V, points to the creation of a strong bond in which the inhibitor is a donor and the metal is an acceptor. Reduction of the rate of cathodic reaction is the result of a decrease in oxygen concentration or formation of the adsorption film, which constitutes a diffusion barrier for oxygen.

See Fig. 1. Electrochemical behavior of CORNOX inhibitors.

EXPERIMENTAL

The bulk of work described in this paper, deals with nitrile elastomers. However, examination has also been made of the effects of CORNOX addition to Neoprene, EPDM, SBR and Isoprene elastomers. The results of those investigations have been reported in previous publications (3,4).

As a best approach to the selection of test compounds, it was decided to use a typical combination of a polymer and compounding ingredients that show random corrosion performance. Therefore, comparative corrosion tests were conducted on test recipes with and without CORNOX additives. Selected was Garlock’s control compound, based on Hycar 1042 elastomer. The compound specifications including GMRP reading, are given on Table I.

Table I - Compound Specification

All test recipes were milled following normal laboratory procedures with special attention to prevent contamination. The test slabs were molded at 350°F for 8 minutes and prepared for corrosion tests in accordance with standard procedure described in (1). CORNOX samples were given designation EXP 4639 and included 5 parts per hundred addition of CORNOX 13-A-II formulation.

The summary of experimental results after exposure to standard test media is given on Table II - Corrosion Test Results

The method employed to evaluate corrosive characteristics of test compounds, was the General Motors Engineering Standard GM-9003-P. This test gives reproducible result with a minimum of equipment. Results are expressed in terms of a rating system wherein exposed test plates are compared to five corrosion “Standards” showing graduated degrees of corrosion. Ideally, the seal material should have a zero rating in regards to its corrosive effect on steel. Realistically, however, a maximum allowable corrosion rating is usually specified for each seal application.

The method consists of compressing the rubber specimen between two metal plates and exposing the assembly to the test environment. Steel plates and rubber specimen are cut to specified dimensions and cleaned prior to exposure to eliminate the possibility of distorting the corrosion results due to impurities and fingerprints on the test surfaces. At the conclusion, the sample is removed from the test chamber, disassembled and inspected. The plates with adhered elastomers are dipped in naphtha, polished with crocus cloth and their appearance compared with corrosion standards.

It is very apparent that the action of CORNOX does substantially inhibit the effect of corrosion in the various EP lubes, transmission oils and standard test fluids. The ratings noted above do point out that there is an extraction effect when CORNOX is exposed to certain additives that are inherent properties of various fluids. However, in all cases the ratings were below those obtained when CORNOX was not added.

In addition to ferrous metals, investigations were performed on three of the most widely used non-ferrous metals; aluminum, brass and bronze.

All of the tests conducted on non-ferrous metals were performed using the same General Motors Engineering Standard GM-9003-P, and the same rating procedure.

(See Table III - Corrosion Test Results on Non-Ferrous Metals)

* CORNOX is a combination of Northern Instruments proprietary corrosion inhibitors.

Table I - Compound Specifications

Customer material number (GM 6009-M)	N. 72.10.C4. DA 102, DX 102 DZ 300, EX 201, EZ 004
Hardness (GM-9004-P)	72 ± 5 I.R.H.D.
Corrosion Rating (GM-9003-P)	3
Aging Test (ASTM D-471)	70 hrs. @ 212°F.
Test Media	TL 6673
Hardness Change (GM-9004-P)	-10 to 0 7TS
Volume Change (ASTM D-4721)	0 to +10 6/o

Table II - Corrosion Test Results

Test Media (70 hrs. 212°F.)	Rating	
	Control	EXP4639 (CORNOX)
Humidity, (GMRP)	4-5	0-1
Oil MS-5644	5	2
Oil Mobil 464	5	1-2
Oil TL-3450	5	4-5
Oil SAE-80	5	0
Oil #9627	5	1

Oil Dextron	5	0
Oil ASTM #1	5	3
Oil ASTM #3	5	0
Oil #5491	5	0

The results indicate that CORNOX was protective to non-ferrous metals under investigation. This is in good agreement with proposed corrosion inhibiting mechanism, which, as discussed above, involves electrochemical reactivity with dissimilar metal substrates.

The retention of mechanical properties is of great importance for acceptance of inhibited seal formulation. Therefore, all CORNOX samples were carefully examined to determine possible adverse effect. The summary of results of physical tests is given on Tables IV and V.

In addition to standard physical tests, it was decided to mold actual production parts (#2 and #3 seals, Figure 3), and compare their performance with the known performance of control samples. The results show that the seals based on CORNOX performed equally as well as standard controls. Under standard test conditions leakage of the test fluid (hot lubricating oil TL-3450) occurred after 300 hours for both samples, which is acceptable to the specifier.

RESULTS AND DISCUSSIONS

We believe that adding to elastomers, common structural components of every engineered system, inhibitive properties in relation to metals, will open a new approach in corrosion control, which we call a "functional inhibition". Corrosion inhibitors have been used to treat water in cooling systems and to impregnate wrapping paper, but they have not been taken into use to a great extent, even in the cases where their usefulness should be obvious. One of these cases certainly is the compounding into rubbers, and utilizing the rubber parts as permanent emitters of inhibiting material.

Having brought this method to a successful start, a number of potential applications have occurred, interesting results have been obtained and valuable experiences gathered.

REFERENCES

1. H.E. Trexler, G.A. Illka and P.J. Weiss, *Appli. Pol. Sci.*, 8, No. 2 (1964)
2. B.F. Goodrich Company, *Hycar Technical Newsletter*, 11, No. 2 (1962)
3. B.A. Miksic and D. P. Stern, "4th European Symposium on Corrosion Inhibitors", University of Ferrara, 1975, pp. 136-149.
4. B.A. Miksic, "Corrosion/76", National N.A.C.E. Meeting, Houston, paper No. 70, March 1976.

Table III - Corrosion Test Results on Non-Ferrous Metals

<u>Metal</u>	<u>Control</u>	<u>Rating</u>	<u>EXP 4639 (CORNOX)</u>
Aluminum 2024	5		1
Brass (ASTM B 36)	5		0
Bronze (bearing)	5		0

Table IV - Original Properties, Cured 8 Minutes at 350°F.

	<u>Control</u>	<u>CORNOX</u>
1. Hardness, Shore "A"	78	75
2. Tensile strength, psi	1683	1758
3. Elongation, %	317	373
4. Modulus at 100%	882	775
5. Specific gravity	1.40	1.40
6. Compression set, Method "B"	44.7	45.50
7. Corrosion, GM-9003-P	4-5	0-1

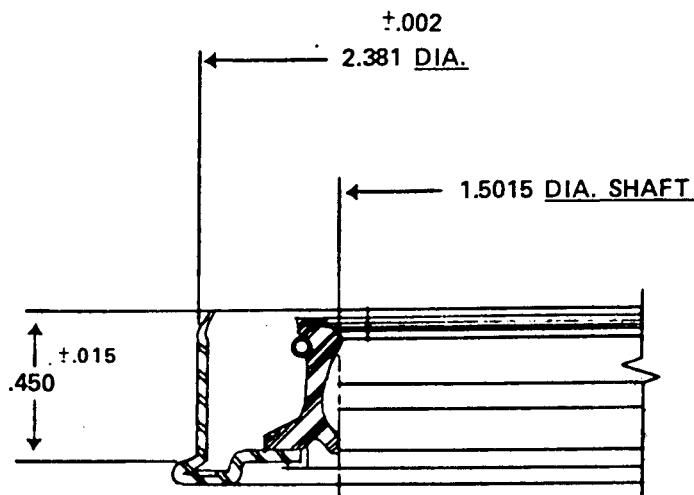


Fig. 3 - Experimental oil seal

Table V - Effect of CORNOX on Properties, Cured 8 Minutes at 350°F.

1. Hardness Change, % Max
2. Tensile Change, % Max
3. Elongation Change, % Max
4. Volume Change, % Max
5. Surface Condition

	Air Oven ASTM-D-573		ASTM #1 Oil		ASTM #3 oil		ELCO ASTM- 28 80		Oil (1) Dextron II		Oil Exxon 5491		Oil Texaco-9622		Fuel "B" (2)		Oil Texaco-3450		Oil Mobil-644		Oil MS-5644		
	Con- trol	COR- NOX	Con- trol	COR- NOX	Con- trol	COR NOX	Con- trol	COR NOX	Con- trol	COR NOX	Con- trol	COR NOX	Con- trol	COR NOX	Con- trol	COR NOX	Con- trol	COR NOX	Con-COR trol NOX	Con-COR trol NOX	Con-COR trol NOX	Con-COR trol NOX	
1	+4	+5	+1	+2	-11	-10	-16	-17	+1	+1	-1	-1	-2	-2	-21	-22	-10	-12	+1	-2	0	-1	
2	+2	-3.1	-10.5	-11.9	-21.2	-22.7	-22.3	-27.3	-24.7	-36.3	-16.9	-14.1	-17.8	-16.6	-50.3	-53.2	-30.7	-32.7	-7.6	-8.0	-21.7	-28.8	
3	-14.0	-18.4	-16.0	-9.6	-15.1	-11.1	-16.7	-15.4	-61.0	-73.0	-50.7	-26.2	-31.2	-27.0	-38.2	-31.6	-18.2	-24.3	-15.6	-27.8	-17.6	-16.2	
4	-1.53	-1.84	+14.72	+14.8	+20.8	+21.72	+2.59	+3.37	+3.79	+4.25	+4.4	+4.34	+31.75	+31.56	+19.13		+1.0	+2.6	+5.93	+6.75	
5	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	+19.36	gritty	gritty	OK	OK	OK	OK

* Oil immersion tests performed at 212°F for 70 hours.
 (1) 108 hours at 300°F
 (2) 76 hours at R.T.