ANTIFUNGAL SEALING RINGS - A NEW APPROACH*

P. Dunn and D. Oldfield

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A new approach has been used both in the laboratory and in field trials, to study the development and performance of special Vulcanizates used in sealing applications. The use of conventional, monomeric fungicides has been replaced by polymeric organotin compounds covalcanized into the rubber network. Polychloroprene, acrylonitrile-butadiene rubber and ethylene-propylene terpolymer are three rubbers commonly used in military equipment and these have been shown to covalcanize with tributyltin acrylate in the presence of peroxides to give vulcanizates with a powerful and long-lasting fungicidal action. These rubbers have been evaluated by the use of O-rings to form sealed cavities with ten different materials (two metals, seven plastics and glass), in specially designed assemblies.

Trials held over 3 years in adverse environments have confirmed that the rubbers are compatible with the sheet materials, can be formed into efficient sealing products that will prevent fungal growth, have good performance characteristics, and do not degrade the optical qualities of transparent materials. These rubbers should have applications in military, industrial and commercial equipment.

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1. INTRODUCTION

During World War II and the Vietnam War, fighting on a large scale using modern military equipment occurred over a wide range of environmental conditions. Equipment losses and failures in adverse environments due to corrosion, microbiological attack, hydrolysis and actinic degradation were enormous.

In particular, sensitive optical and electronic military equipment was rapidly rendered unserviceable by the growth of microorganisms such as fungi. This problem is still serious in tropical areas and usually results in the use of elaborate and costly sealing procedures. Upsher (1) has described some of the problems associated with microbial attack on materials.

A common method of sealing sophisticated military, industrial and commercial equipment is by the use of O-rings and similar types of seals. These are only of value if they can be shown to effectively prevent the ingress of fungal growths. Fungicides are often incorporated into these rubbers but usually only have limited lifetimes due to their depletion by hydrolysis, leaching, blooming or evaporation from the rubber surface. In addition, many of the fungicides contain heavy metals such as copper and mercury and these often promote deterioration of substrate materials. Chlorine containing fungicides are prone to cause corrosion of, and adhesion to, metallic components (2).

Fungicides based on organotin compounds usually do not exhibit many of these disadvantages (3). Using a modification of a system developed at MRL to prevent the growth of marine fouling on underwater surfaces (4), we have produced elastomeric vulcanizates which have long-term fungicidal properties and which can be used in sealing applications. Leading references to earlier work on the use of organotins in rubber may be found in previous publications in this series (4). In addition, many reports on the selection of suitable elastomers and the use of O-rings, are available (5-9).
2. ORGANOTIN FUNGICIDES

Van der Kerk (10) showed that organotin compounds of the type Alkyl\textsubscript{3}SnX were very effective fungicides. Commercially used materials include triphenyl and tributyltin oxide, chloride, fluoride and acetate. Triphenyltin acetate, for example, is marketed as a 20% active water-wettable powder called "Brestan" and is used to control blight (Phytophthora infestans) in potatoes (10).

Certain organotin compounds such as tributyltin fluoride can also be incorporated into rubbers and plastics (4,11,12) to prevent marine fouling and also mould growth under damp conditions. Some of the disadvantages of simple incorporation of a fungicide into rubber include, (i) serious retardation of the curing system (ii) possible impairment of the physical properties of the vulcanizate (iii) a wastefully high rate of release of the fungicide and (iv) a limited lifetime for the material.

In order to overcome these drawbacks we have prepared vulcanizates in which the fungicide, in this case tributyltin acrylate (TBTA), is co-vulcanized into the rubber network by the use of a peroxide curing system, an approach which has been discussed in detail elsewhere (4).

The elastomers chosen were polychloroprene (CR), acrylonitrile-butadiene (nitrile; NBR) and ethylene-propylene terpolymer (EPDM) on the basis of their specific properties such as heat resistance, oil resistance and long-term ageing characteristics. All these rubbers are widely used in military equipment for toroidal sealing ring applications (13,14,15). About 5% by weight of TBTA was incorporated into the fungicidal vulcanizate. This is a higher level of fungicide than would normally be used but was selected as curing characteristics and physical properties were not impaired, long-term retention of active material was sought and any problems associated with the material ought then to be revealed.

3. EXPERIMENTAL

3.1 Elastomeric Materials

Experiments were designed using two concentric O-rings to form an enclosed and sealed cavity between selected metallic and non-metallic substrate materials. With each pair of rings used to form the cavity, one contained the fungicide, while the other was used as a control specimen.

The rubber formulations are shown in Table 1 and compounding ingredients in the Appendix. Other compounding materials comparable in chemical composition and activity should be equally satisfactory. TBTA was prepared from bis(tributyltin) oxide and acrylic acid by recognised procedures (16). The formulations were mixed on a 200 mm x 75 mm laboratory 2-roll mill and curing characteristics were determined on a Monsanto Model LSD rheometer. O-rings (4-cavity mould) and test sheets (2-cavity mould, 225 mm x 125 mm x 1.9 mm) were vulcanized in an electrically heated press
at 160°C for 30 min. The preparation and inspection of the O-rings conformed as closely as possible to established standards (17,18). Mechanical properties (Table 1) of test sheets were determined under standard conditions (19,20). The properties of the O-rings were determined on an Instron Model 1026 tensometer using a motorised specimen holder drive unit and standard operating conditions (21-27).

The O-rings were coded thus:

<table>
<thead>
<tr>
<th>Vulcanizate</th>
<th>Control</th>
<th>Fungicidal (5% TBTA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polychloroprene</td>
<td>CR-C</td>
<td>CR-F</td>
</tr>
<tr>
<td>Nitrile</td>
<td>NR-C</td>
<td>NR-F</td>
</tr>
<tr>
<td>Ethylene-propylene</td>
<td>EP-C</td>
<td>EP-F</td>
</tr>
</tbody>
</table>

The dimensions of the circular cross section rings were: control (large ring), external diameter 82.6 mm, internal diameter, 72.0 mm; fungicidal, (small ring) external diameter, 39.6 mm, internal diameter 28.0 mm.

### 3.2 Substrate Materials

The ten metallic, glass and plastics materials used in the assemblies were: aluminium plate (a magnesium-aluminium alloy with good resistance to corrosion by seawater); commercial stainless steel (for discs and hardware); nylon 11, natural; poly(methyl methacrylate) (PMMA), transparent; acrylonitrile-butadiene-styrene (ABS), white; polypropylene, (PP) natural; rigid poly(vinyl chloride) (UPVC), grey; glass reinforced polyester resin (GRP), natural; polycarbonate (PC), transparent; and glass, polished plate. Surface textures of discs were measured using a Taylor Hobson, "Talysurf" instrument (28). The Centre Line Average (CLA) readings were taken at eight random positions on each specimen face using an instrument cut-off of 0.8 mm and a trace length of 3.8 mm. The assessment of fungicidal activity of materials used in the test assemblies was determined by standard techniques (29).

### 3.3 Test Assemblies

Each test assembly (Fig. 1) consisted of a circular aluminium base plate (300 mm diameter x 6 mm thick) with three 20 mm diameter holes equidistantly spaced, 55 mm from the outside edge. Three stacks of ten discs of different materials (each 100 mm diameter and with a 20 mm diameter hole at the centre) were placed so that the holes in the discs were collinear. Between each pair of surfaces, one large control O-ring and one small fungicidal O-ring of the same base rubber were placed concentrically to form an annular cavity sealed by the two rings. Two O-rings were placed similarly on the top of each stack and a top plate, similar to the base plate was added. Each assembly was held together with nine stainless steel bolts. The combinations of O-rings in each of the three stacks per test assembly were CR-C and CR-F, NR-C and NR-F and EP-C and EP-F. The sequence of materials in the assembly is shown in Fig. 2.
During assembly a small disc of nylon 6 (10 mm diameter x 2 mm thick), previously dried in a vacuum over for 24 h at 100°C, was placed in each cavity, in order to monitor uptake of moisture. Hardness of the disc was determined (30) using the Barcol Model GY2-J935 impressor. Each assembly was bolted together, under load, to 85% of the original thickness (15% compression).

### 3.4 Environmental Exposure

One complete assembly and a number of unused O-rings was stored, in the dark, at Maribyrnong, Victoria. One assembly was exposed outdoors at Maribyrnong and another outdoors at J.T.R.U., Innisfail, Queensland ("hot-wet" tropical) at a cleared site near the jungle. These assemblies were exposed in a horizontal position, about 1 m above the ground and were protected from direct solar radiation by a 400 mm diameter opaque plastics sheet fixed 25 mm above the assembly.

A fourth assembly was submerged in a tank of flowing seawater at Naval Dockyard, Williamstown, Victoria. The assemblies were exposed for 3 yr at each site. Typical meteorological data for a 5 yr period are given in Table 2.

With six different rubbers (3 control, 3 fungicidal), ten different materials, two types of cavities (open and closed) and four environmental exposure conditions, the number of variables totalled 480.

### 3.5 Assessment

Assemblies returned from exposure and controls were examined for any cracking of rings and for the presence of fungal growth. On dismantling, adhesion between rings and substrates was assessed and the hardness of each small nylon indicator disc measured. The axial and radial thicknesses of each ring were measured 0.5 h, 24 h and 48 h after dismantling. Hardness of rings was measured after 24 h (31) and tensile properties after 48 h. Substrate materials were examined for signs of stress cracking and corrosion and annular cavities for signs of fungal growth or changes in transparency of particular materials. Residual fungicidal activity of rings was assessed.

### 4. RESULTS AND DISCUSSION

#### 4.1 General

In order to perform satisfactorily in a sealing device, rubbers must remain stable over long periods under static stress and adverse conditions such as high and low temperatures, vibration, shock, sunlight and ozone and in the presence of a wide range of chemicals such as water, fuels, lubricants, solvents and hydraulic fluids. Mechanical properties, particularly compression set and hardness should remain stable in order to ensure long-term sealing efficiency. In optical devices rubbers must not generate volatile chemical compounds likely to sublime onto glass components and cause loss of transparency. When equipment has to be dismantled for modification or servicing, adhesive strength between rubber and substrate should
be weak. All these factors were assessed as part of the trial.

The concept we have developed involves the use of high quality, peroxide-cured rubbers known to be suitable for use in military applications and the replacement of conventional monomeric, low molecular weight fungicides by high molecular weight active organotin compounds covalcanized into the rubber network.

4.2 Visual Examination

Rings in the indoor control assembly showed no evidence of ozone cracking or deterioration. A slight texturing of the surface of the rubbers in contact with glass reinforced plastics (GRP) was evident in all assemblies.

At the temperate site, the large nitrile rings, as expected, showed extensive ozone cracking on the exposed circumference. There was no cracking of the small fungicidal nitrile ring or the polychloroprene or ethylene-propylene terpolymer rings. Rubbers exposed in assemblies in the tropics gave similar results and this is in agreement with published data (32). All assemblies exposed outdoors showed severe contamination by dirt and other debris.

On dismantling the assemblies the adhesive strength between rings and substrates was assessed. No marked differences were evident between control and fungicidal rings in any of the assemblies and all rubbers had very weak bonds to nylon and to polypropylene.

For assemblies not immersed in seawater polychloroprene rubber showed strong bonding to both plate glass and GRP and weak bonding to ABS. Nitrile rubber showed strong bonding to GRP and UPVC, and ethylene-propylene terpolymer displayed strong bonding to GRP and to polycarbonate. For the assembly immersed in seawater, the only strong bonds identified were, between all rubbers and stainless steel (probably accentuated by the presence of corrosion products), nitrile rubber to ABS and GRP and ethylene-propylene rubber to ABS and UPVC.

The assembly immersed in seawater for 3 yr was heavily encrusted with barnacles and other marine fouling organisms (Fig. 3). The annular cavities between the aluminium cover plates and the metal discs in each stack were filled with a white crystalline corrosion product, identified as mainly aluminium salts. The rubber rings forming these cavities were slightly swollen and, in some cases, deformed. There was severe corrosion of the cover plates (Fig. 4) where they had been in contact with the rings, mainly due to crevice corrosion (33).

All rings in contact with glass and plastics were in good condition, and the sealed cavities were clean and dry. Some minor hairline cracking was present on the control nitrile rings.

There were no signs of stress cracking or crazing on any of the plastic materials. This is significant for polycarbonate and PMMA and indicates that all of the rubbers can be used under stress, in contact with these transparent materials for long periods.
4.3 Sealing Efficiency

It has been shown (34) that the indentation hardness (Barcol) of sheets of nylon 6 is dependent on the water content. For a sheet of specific thickness, a calibration graph as shown in Fig. 5, can be constructed to relate hardness and water content. By placing an indicator disc of nylon, dried to zero water content, in each sealed cavity and measuring the hardness of the disc when the assembly was dismantled, an indication of moisture content of the nylon was obtained.

Dried indicator discs were exposed to relative humidities of 0%, 30%, 52% and 100% at 23°C and also to a laboratory atmosphere without humidity control at the same temperature during the dry summer period. The percentage weight increase of the discs is plotted against the time of exposure in Fig. 6. The water content of each indicator disc in the trial, derived from the measured hardness and the calibration graph, Fig. 5, is shown in Table 3.

The water content of indicator discs in the control assembly was about 2% and for assemblies exposed under temperate and tropical conditions it was always less than 3%, suggesting good sealing efficiency. As expected, higher equilibrium water contents were found in discs from the assembly immersed in seawater - the maximum result was 5.3%. Cavities sealed with polychloroprene and ethylene-propylene rubbers had lower moisture contents than those sealed with nitrile rubbers.

As the average water content of indicator discs in the control assembly was about 2%, and from Fig. 6 discs exposed under ambient conditions gain about 2% moisture in 50 days, the sealing obviously has a marked effect on the rate of diffusion of moisture into the cavities over the 3 yr trial period. The absorption of water by elastomers has been studied (35,36) and the equilibrium water absorption by gum vulcanizates at 88% r.h. was estimated as 0.75% for SBR, 0.5% for natural rubber and 0.25% for butyl rubber. By contrast, polychloroprene rubbers continued to absorb water due to the metal oxide curing system, with a value of 1.9% being reported after 2 d. In the present case we are concerned with the transmission of moisture through a compressed rubber ring, and it appears that the three rubbers give similar performance.

The average relative humidity for the temperate and for the tropical sites is 55% and 82% respectively (Table 2). Under these conditions the equilibrium moisture value for the indicator disc is about 7% and 8% respectively (Fig. 6). As indicator discs after 3 yr in trial assemblies had moisture values much less than equilibrium value for discs with free access to moisture, effective sealing must have been maintained.

For the assembly immersed in seawater one side of each ring was exposed to water for 3 yr, and the average moisture content of indicator discs was about 5% (excluding metal - metal cavities subjected to crevice corrosion). In the long term, a relative humidity of 30% or less would produce a similar equilibrium value. This indicates that the average humidity in the sealed cavities under marine immersion conditions was substantially less than 50%.
4.4 Antifungal Performance

Rubbers containing co-vulcanized TBTA are designed to slowly release an organotin compound known to be toxic to most fungi usually found in tropical areas. As shown previously (4), although the organotin groups are firmly bound into the rubber network, when water diffuses into the rubber reactions occur which cause the release of fungicidally active compounds as shown below:

\[
\text{Rubber} \quad \text{Peroxide} \quad \text{Rubber} \quad \text{TBTA} \\
\text{Hydrocarbon} \quad \text{Free} \quad \text{Free} \quad \text{Radical} \quad \text{Radical} \\
\]

\[
\begin{align*}
\text{CH}_3 & \quad + \quad \text{RO}^+ \\
\text{CH}_3 & \quad \rightarrow \quad \text{C}^+ & \quad + \quad \text{CH}_2 = \text{CH} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{Rubber} & \quad \text{Peroxide} & \quad \text{Rubber} & \quad \text{TBTA} \\
\text{Hydrocarbon} & \quad \text{Free} & \quad \text{Free} & \quad \text{Radical} & \quad \text{Radical} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 & \quad \left(\text{CH}_2 - \text{C} - \text{CH}_2\right) \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{COOSnBu}_3 \\
\text{CH}_2 & \quad \text{COOSnBu}_3 \\
\end{align*}
\]

Covulcanized Rubber

\[
\begin{align*}
\text{H}_2\text{O} & \quad \left(\text{CH}_2 - \text{C} - \text{CH}_2\right) \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CO}_2\text{H} \\
\text{CH}_2 & \quad \text{COOSnBu}_3 \\
\end{align*}
\]

Bis(tributyltin) oxide

Active Fungicide

This process is known to be slow and ensures that active material is not rapidly depleted from the rubber. When cavities are first sealed by the use of covulcanized O-rings, any low molecular weight residual organotin fungicide will volatilise and give immediate short-term protection. Ingress of any moisture will initiate hydrolysis of active organotin groups and release bis(tributyltin) oxide into the cavity. In the absence of moisture no change in the organotin polymer will occur.

No fungal contamination was observed inside any sealed cavity of the assemblies (Fig. 7). The assembly from the tropical area which would have been most susceptible to fungal attack, had slight fungal growth present on
the outer exposed surfaces of the control rings, but none on or near the inner fungicidal rings. Microscopic examination of all the materials inside the sealed cavities failed to show the presence of any microorganisms. The small fungicidal rings were still biologically active after the 3 yr trial period.

It has been reported that to promote adequate sealing a surface finish better than 0.8 \( \mu m \) \( Ra \) is desirable (37). Table 4 indicates that, with the exception of one side of the stainless steel and glass reinforced plastics discs, all substrates conformed to the recommended finish. The adequate finish of the substrates, combined with the durability of the rubber O-rings and the plastics materials all contributed to sealing efficiency and lack of fungal growth inside sealed cavities.

For cavities containing transparent substrate materials there was no evidence of condensation of fungicide on any internal surface and no loss of transparency. This is particularly significant if optical devices are to be protected from fungal attack.

As sealed cavities made by the combination of O-rings and planar surfaces can be protected by the use of covalcanized fungicides, it is predicted that the use of similar rings located in traditional grooves will be even more effective in preventing ingress of fungal growths.

4.5 Assessment of Mechanical Properties

Meyers and Wenrick (38) have reported on the effect of test piece geometry on mechanical properties. The results of our investigation comparing O-rings and test pieces from standard sheets are given in Table 5. This enables a relationship to be established between materials used in long-term trials and original properties of vulcanizates.

The effect of size of O-rings (some specially moulded) was also investigated (Table 6). In all cases the tensile strength measured on large rings was greater than that of the same rubber measured on small rings. For the same size rings, rubbers containing organotin fungicide had higher tensile strengths than control rubbers.

The excellent performance of the peroxide curing system to accelerated ageing in air and in water, is confirmed by the results given in Table 7.

4.6 Trial Results - Mechanical Properties

The tensile strength, elongation at break and compression set results for O-rings used in the trial are given in Figs. 8, 9 and 10 respectively. In Figs. 8 and 9, "original" indicates unstressed rings, stored unassembled in the dark at 23°C. All other results are for rings removed from assemblies.

Properties of unstressed rings and those held under compression in the control assembly were similar for each rubber. In confirmation of accelerated ageing results, the fungicidal polychloroprene rubber, CR-F, showed major changes in properties as a result of water immersion. This is not unexpected for this polymer.
All the large rings (CR-C, NR-C and EP-C) were more liable to attack by ozone and to deterioration by sunlight than the small rings. The lower tensile strength values observed for the nitrile rings at the temperate and tropical sites, compared with original values, reflects the effect of ozone cracking on the exposed surface of the rings. This deterioration did not occur in rings immersed in seawater due to exclusion of ozone. The excellent long-term resistance to ageing of ethylene-propylene rubbers, has been confirmed.

Elongation at break properties, in general, followed similar trends compared to tensile strength. The good retention of elongation at break of nitrile rubbers immersed in seawater again reflects the protection of the surface from attack by ozone. Changes in elongation at break can be used as a measure of the extent of deterioration of vulcanizates. The generally good values for the fungicidal O-rings, indicates that addition of tributyltin acrylate is not in any way detrimental to long-term performance.

Compression set results (Fig. 10) offer important information on long-term sealing characteristics. The "original" results were obtained by conventional methods (39) from standard compression set test pieces, evaluated at 70°C for 24 h. Measurements on rings were made 0.5 h, 24 h and 48 h after release from the assembly and were averaged for all O-rings of a particular type of rubber for each exposure site.

The drop in compression set value from 0.5 h to 24 h indicates the recovery characteristics of the rubber. Rubbers with high compression set values at 0.5 h often show high recovery rates. The two polychloroprene rubbers, CR-C and CR-F, exhibited good compression set results despite being compressed 15% for 3 yr. For the control assembly the value for CR-C (48 h recovery) was 20%. The presence of covulcanized TBTA had little effect on overall results. However, compression set values for both rubbers exposed in the tropics were higher than at other sites.

With nitrile rubber, the presence of TBTA resulted in improved compression set characteristics. The difference between the short-term conventional compression set value and that of the control O-ring assembly was greater for nitrile rubber than for polychloroprene. Conventional results do not relate well to long-term performance.

Ethylene-propylene terpolymers showed large values of compression set after 0.5 h recovery but these reduced to levels close to conventional short-term values after recovery for 48 h. Incorporation of TBTA had no deleterious effect on compression set value in EPDM rubbers.

Moakes (40,41) and Morrell and Watson (42) have reported the results of compression set measurements on annular specimens after 15 yr storage in temperate and tropical (at JTRU, Innisfail) areas. They concluded that "it seems that standard type compression set tests in which the rubber is only compressed for up to 24 h, are inadequate to predict behaviour under long-term compression". Our results agree with this conclusion and confirm that all the rubbers used in our trials should be suitable for use in long-term sealing applications.
None of the O-rings showed marked changes in hardness as a result of exposure (Table 8).

5. CONCLUSIONS

The performance of elastomeric O-rings produced from three different synthetic rubbers containing covulcanized tributyltin acrylate as a long-lasting fungicide, has been assessed in the laboratory and in field trials, over 3 yr. Sealed cavities formed between the O-rings and glass, seven different plastics, stainless steel and aluminium remained dry and free from microbial growth during exposure to several adverse environments.

The long-term compression set of the O-rings was greater than predicted from conventional short-term tests at elevated temperature. Other mechanical properties were not greatly affected by the trial exposures under 15% compression. Certain combinations of elastomers and plastics would not be recommended for applications where ease of separation after long periods of compression was important. The elastomers did not promote stress cracking in any of the plastics and optical properties of transparent materials were unchanged. The incorporation of the organotin fungicides into the rubbers effectively prevented fungal contamination of the O-rings and adjacent areas. This technique can be used with most hydrocarbon rubbers.

6. ACKNOWLEDGEMENTS

Thanks are due to Officer-in-Charge, JTRU, Innisfail for arranging the exposure of trial specimens, to Mr. F.J. Upsher, MRL for assessment of fungal activity, to Mr. S. Mesten, MRL for the determination of mechanical properties and to Metrology Group, MRL for measurements on surface finish.

REFERENCES


## Table 1

**Rubber Formulations for Use in O-Rings**

<table>
<thead>
<tr>
<th>Compounding Ingredients</th>
<th>Rubber Designation</th>
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<tr>
<td>Polychloroprene (CR)</td>
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<tr>
<td>Butadiene-acrylonitrile (NBR)</td>
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<tr>
<td>Ethylene-propylene terpolymer (EPDM)</td>
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<td>Carbon black</td>
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<td>Zinc mercaptobenzimidazole</td>
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<tr>
<td>Tributyltin acrylate</td>
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**Original Properties (a)**

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</tr>
<tr>
<td>Compression set, 24 h at 70°C, %</td>
<td>13</td>
<td>15</td>
<td>12</td>
<td>11</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>Cold flex temperature, °C (b)</td>
<td>-32.5</td>
<td>-36.5</td>
<td>-22.5</td>
<td>-23.5</td>
<td>-63</td>
<td>-65</td>
</tr>
</tbody>
</table>

(a) Determined on moulded test sheets.

(b) B.S.2571-1963 (Clash and Berg method).
TABLE 2

METEOROLOGICAL DATA FOR THE FIVE YEAR PERIOD, 1970-74

<table>
<thead>
<tr>
<th>Property</th>
<th>Melbourne, Vic. (Temperate)</th>
<th>Innisfail, Qld. (Hot-Wet, Open)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude, S</td>
<td>37° 49'</td>
<td>17° 32'</td>
</tr>
<tr>
<td>Longitude, E</td>
<td>144° 58'</td>
<td>145° 58'</td>
</tr>
<tr>
<td>Elevation, m</td>
<td>34.7</td>
<td>39.6</td>
</tr>
<tr>
<td>Temperature, °C (Average Daily Max)</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>Relative Humidity, % (Average Index)</td>
<td>55</td>
<td>82</td>
</tr>
<tr>
<td>Total Rainfall, mm</td>
<td>3597</td>
<td>18145</td>
</tr>
<tr>
<td>Total Sun, h</td>
<td>11406</td>
<td>11723</td>
</tr>
</tbody>
</table>
TABLE 3

WATER CONTENT (\(\%, \text{w/w}\)) OF NYLON INDICATOR DISCS AFTER STORAGE FOR 3 YR

<table>
<thead>
<tr>
<th>Cavity Designation (a)</th>
<th>Control</th>
<th>Temperate</th>
<th>Tropical</th>
<th>Marine Immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CR (b)</td>
<td>NR</td>
<td>EP</td>
<td>CR</td>
</tr>
<tr>
<td>A (Top)</td>
<td>1.8</td>
<td>1.8</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>B</td>
<td>1.4</td>
<td>2.2</td>
<td>1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>C</td>
<td>1.6</td>
<td>2.1</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>D</td>
<td>1.8</td>
<td>2.1</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>E</td>
<td>2.0</td>
<td>2.0</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>F</td>
<td>1.8</td>
<td>2.1</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>G</td>
<td>1.8</td>
<td>2.0</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td>H</td>
<td>2.0</td>
<td>2.1</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>I</td>
<td>1.8</td>
<td>2.0</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>J</td>
<td>1.8</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>K (Base)</td>
<td>2.1</td>
<td>2.1</td>
<td>2.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>

(a) See Fig. 2.

(b) Annular cavity sealed by type of rubber as designated. Thus CR (polychloroprene) cavity formed by CR-C large ring and CR-F small ring.

(c) Not applicable due to corrosion products in the cavity.
# Table 4

## Surface Texture of Discs

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Texture, μm Ra&lt;sup&gt;(a)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Side 1</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.3</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>0.4</td>
</tr>
<tr>
<td>Nylon 11</td>
<td>0.6</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>0.1</td>
</tr>
<tr>
<td>Acrylonitrile-butadiene-styrene</td>
<td>0.05</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.7</td>
</tr>
<tr>
<td>Rigid poly(vinyl chloride)</td>
<td>0.6</td>
</tr>
<tr>
<td>Glass-reinforced polyester</td>
<td>0.9</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>0.2</td>
</tr>
<tr>
<td>Glass</td>
<td>0.005</td>
</tr>
</tbody>
</table>

(a) Centre Line Average (CLA) readings.
TABLE 5

COMPARISON OF DUMBELL AND O-RING TEST SPECIMENS

<table>
<thead>
<tr>
<th>Rubber Designation</th>
<th>Tensile Strength, MPa</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dumbell (a)</td>
<td>O-Ring (b)</td>
</tr>
<tr>
<td>CR-C</td>
<td>19.2</td>
<td>17.3</td>
</tr>
<tr>
<td>CR-F</td>
<td>15.1</td>
<td>12.9</td>
</tr>
<tr>
<td>NR-C</td>
<td>19.4</td>
<td>16.4</td>
</tr>
<tr>
<td>NR-F</td>
<td>19.2</td>
<td>13.5</td>
</tr>
<tr>
<td>EP-C</td>
<td>14.7</td>
<td>13.6</td>
</tr>
<tr>
<td>EP-F</td>
<td>15.4</td>
<td>13.5</td>
</tr>
</tbody>
</table>

(a) Determined at time of moulding.

(b) Determined after indoor storage, unstressed, for 3 yr.
### TABLE 6

EFFECT OF RING SIZE ON MECHANICAL PROPERTIES

<table>
<thead>
<tr>
<th>Rubber Designation</th>
<th>Internal diameter, (a) mm</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
<th>Hardness, IRHD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-C(^{(b)})</td>
<td>28</td>
<td>7.8</td>
<td>200</td>
<td>70</td>
</tr>
<tr>
<td>CR-C</td>
<td>72</td>
<td>17.3</td>
<td>270</td>
<td>70</td>
</tr>
<tr>
<td>CR-F</td>
<td>28</td>
<td>12.9</td>
<td>220</td>
<td>73</td>
</tr>
<tr>
<td>NR-C(^{(b)})</td>
<td>28</td>
<td>12.9</td>
<td>320</td>
<td>60</td>
</tr>
<tr>
<td>NR-C</td>
<td>71</td>
<td>16.4</td>
<td>330</td>
<td>59</td>
</tr>
<tr>
<td>NR-F</td>
<td>28</td>
<td>13.5</td>
<td>360</td>
<td>58</td>
</tr>
<tr>
<td>EP-C(^{(b)})</td>
<td>28</td>
<td>12.0</td>
<td>850</td>
<td>51</td>
</tr>
<tr>
<td>EP-C</td>
<td>71</td>
<td>13.6</td>
<td>840</td>
<td>52</td>
</tr>
<tr>
<td>EP-F</td>
<td>28</td>
<td>13.5</td>
<td>700</td>
<td>54</td>
</tr>
</tbody>
</table>

(a) The axial and radial thickness of all rings varied within the limits 4.6 to 4.9 mm.

(b) Specially moulded for this evaluation.
### Table 7

**Accelerated Ageing of O-rings**

<table>
<thead>
<tr>
<th>Rubber Designation</th>
<th>Tensile Strength, MPa</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Air, 7d at 70°C</td>
</tr>
<tr>
<td>CR-C(^{(a)})</td>
<td>17.3</td>
<td>17.2</td>
</tr>
<tr>
<td>CR-F(^{(b)})</td>
<td>12.9</td>
<td>14.8</td>
</tr>
<tr>
<td>NR-C(^{(a)})</td>
<td>16.4</td>
<td>18.6</td>
</tr>
<tr>
<td>NR-F(^{(b)})</td>
<td>13.5</td>
<td>13.9</td>
</tr>
<tr>
<td>EP-C(^{(a)})</td>
<td>13.6</td>
<td>12.8</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Large O-rings, internal diameter, 72 mm.

\(^{(b)}\) Small O-rings, internal diameter, 28 mm.
TABLE 8

HARDNESS CHANGES DURING EXPOSURE

<table>
<thead>
<tr>
<th>Rubber Designation</th>
<th>Original Hardness, IRHD</th>
<th>Mean change in hardness, %</th>
<th>Control</th>
<th>Temperate</th>
<th>Tropical</th>
<th>Marine Immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-C</td>
<td>70</td>
<td></td>
<td>+1.4</td>
<td>+1.4</td>
<td>+2.9</td>
<td>0</td>
</tr>
<tr>
<td>CR-F</td>
<td>73</td>
<td></td>
<td>0</td>
<td>0</td>
<td>-1.4</td>
<td>-5.5</td>
</tr>
<tr>
<td>NR-C</td>
<td>59</td>
<td></td>
<td>0</td>
<td>-1.7</td>
<td>+1.7</td>
<td>-5.1</td>
</tr>
<tr>
<td>NR-F</td>
<td>58</td>
<td></td>
<td>0</td>
<td>-1.7</td>
<td>+5.2</td>
<td>-3.4</td>
</tr>
<tr>
<td>EP-C</td>
<td>52</td>
<td></td>
<td>+1.9</td>
<td>0</td>
<td>+1.9</td>
<td>-3.8</td>
</tr>
<tr>
<td>EP-F</td>
<td>54</td>
<td></td>
<td>0</td>
<td>0</td>
<td>+3.7</td>
<td>-1.9</td>
</tr>
</tbody>
</table>
# Appendix

## Materials

1. **Compounding Materials**
   - Bis(trIBUTYLTIN) oxide
   - Butadiene-acrylonitrile rubber
   - Carbon black
   - Diaryl-\(p\)-phenylenediamine
   - Dicumyl peroxide (40% active)
   - Ethylene-propylene terpolymer
   - 2-Mercaptomidazoline
   - Polychloroprene rubber
   - Trimethylolpropane trimethacrylate
   - Zinc mercaptobenzimidazole

2. **Substrate Materials**
   - Acrylonitrile-butadiene-styrene
   - Aluminium
   - Glass
   - Glass-reinforced polyester
   - Nylon 11
   - Polycarbonate
   - Poly(methyl methacrylate)
   - Polypropylene
   - Rigid poly(vinyl chloride)
   - Stainless steel

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBTO</td>
<td>Osta Chemicals Ltd.</td>
</tr>
<tr>
<td>Butakon A3003</td>
<td>ICI Aust. Ltd.</td>
</tr>
<tr>
<td>Acarb 600</td>
<td>Australian Carbon Black Pty.Ltd.</td>
</tr>
<tr>
<td>Akroflex AZ</td>
<td>Du Pont Inc.</td>
</tr>
<tr>
<td>Dicup 40C</td>
<td>Hercules Powder Co.</td>
</tr>
<tr>
<td>Nordel 1440</td>
<td>Du Pont Inc.</td>
</tr>
<tr>
<td>NA-22</td>
<td>Du Pont Inc.</td>
</tr>
<tr>
<td>Neoprene WRT</td>
<td>Du Pont Inc.</td>
</tr>
<tr>
<td>SR 350</td>
<td>Sartomer Resin Inc.</td>
</tr>
<tr>
<td>ZMB</td>
<td>Bayer Australia Ltd.</td>
</tr>
<tr>
<td>Cycolac</td>
<td>Marbon Chemicals Ltd.</td>
</tr>
<tr>
<td>Alloy M57S-H34</td>
<td>Australuco Aluminium Co.</td>
</tr>
<tr>
<td>Polished plate</td>
<td>Commercial supplier</td>
</tr>
<tr>
<td>GRP</td>
<td>Melbourne Fibreglass Panels</td>
</tr>
<tr>
<td>Rilsan</td>
<td>Cadillac Plastics (Aust.) Pty.Ltd.</td>
</tr>
<tr>
<td>Lexan</td>
<td>General Electric Co.</td>
</tr>
<tr>
<td>Perspex</td>
<td>ICI Aust. Ltd.</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>Shell Chemical (Aust.) Pty.Ltd.</td>
</tr>
<tr>
<td>Darvic</td>
<td>ICI Aust. Ltd.</td>
</tr>
<tr>
<td>Style 18/8</td>
<td>Commercial supplier</td>
</tr>
</tbody>
</table>
FIG. 1(a) - Typical stack during assembly (CR-C, CR-F).
FIG. 1(b) - Complete assembly (Control).
FIG. 2 - Sequence of materials used in each stack in each test assembly.
FIG. 3 - Assembly after immersion in seawater for 3 yr.
FIG. 4 - Aluminium base plate showing the effects of crevice corrosion -
(a) before cleaning
(b) after cleaning.
FIG. 5 - Relationship between Barcol hardness of nylon indicator discs and water content determined by weight increase.

WATER UPTAKE OF NYLON DISCS

RELATIVE HUMIDITY AS SHOWN

FIG. 6 - Water uptake of nylon indicator discs.
FIG. 7 - Sealed cavities on dismantling - after 3 yr exposure, showing absence of fungal growth and location of nylon indicator disc.

(a) Temperate, rubber NR-C, NR-F, cavity D, ABS.
(b) Tropical, rubber NR-C, NR-F, cavity D, ABS.
FIG. 7 - Sealed cavities on dismantling - after 3 yr exposure, (cont.) showing absence of fungal growth and location of nylon indicator disc.

(c) Marine immersion, rubber NR-C, NR-F, cavity D, ABS.
TENSILE STRENGTH OF 'O' RINGS

<table>
<thead>
<tr>
<th></th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-C</td>
<td>18</td>
</tr>
<tr>
<td>CR-F</td>
<td>15</td>
</tr>
<tr>
<td>NR-C</td>
<td>12</td>
</tr>
<tr>
<td>NR-F</td>
<td>9</td>
</tr>
<tr>
<td>EP-C</td>
<td>6</td>
</tr>
<tr>
<td>EP-F</td>
<td>3</td>
</tr>
</tbody>
</table>

FIG. 8 - Tensile strength of O-rings after 3 yr exposure.

ELONGATION AT BREAK OF 'O' RINGS

<table>
<thead>
<tr>
<th></th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-C</td>
<td>900</td>
</tr>
<tr>
<td>CR-F</td>
<td>600</td>
</tr>
<tr>
<td>NR-C</td>
<td>300</td>
</tr>
<tr>
<td>NR-F</td>
<td>21</td>
</tr>
<tr>
<td>EP-C</td>
<td>8</td>
</tr>
<tr>
<td>EP-F</td>
<td>2</td>
</tr>
</tbody>
</table>

FIG. 9 - Elongation at break of O-rings after 3 yr exposure.
FIG. 10 - Compression set of O-rings after 3 yr exposure - the three steps in each column represent compression set values after 0.5 h, 24 h and 48 h recovery periods.
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