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CORROSION OF BRASS-RETAINER BALL BEARINGS

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BRASS-RETAINER BALL BEARINGS

INTRODUCTION

For the last two years considerable difficulty has been experienced by ball-bearing manufacturers, military laboratories, and maintenance depots from the corrosion of steel balls and races in brass-retainer ball bearings during storage. This corrosion has been duplicated in the laboratory, and the corrosion product analyzed. A test method suitable for study of this type of corrosion has been derived. The mechanism by which this corrosion occurs has been investigated and methods of alleviating this type of corrosion have been evolved.

ORIGIN OF PROBLEM

Corrosion in the form of fine specks was observed on the steel parts of brass-retainer ball bearings after storage in rooms controlled at 70° to 80°F and 30 to 40 percent relative humidities. The oil used on these bearings previous to packaging and storage was Specification AN-0-11 Aircraft Instrument (Low Volatility) Synthetic Lubricating Oil. Corrosion of a similar nature was later reported to occur when brass-retainer bearings were packaged with Specification 14-0-20 (Ord) Instrument (Synthetic) Lubricating Oil.

At a still later date the Naval Air Station, Norfolk, Virginia, reported that the same general type of corrosion had been observed on bearings packaged and stored with Specification AN-0-6a General Purpose, Low Temperature, Petroleum Lubricating Oil. Thus corrosion of brass-retainer ball bearings is general to these bearings whether in contact with petroleum or with synthetic lubricants and is not necessarily specific to diester oils. Laboratory tests, to be discussed later, substantiate these observations.

LABORATORY INVESTIGATION

Duplication of this type of corrosion in the laboratory proved difficult and long periods often elapsed before corrosion appeared on test specimens. The balls and races used in the ball bearings were of SAE 52100 steel; the brass retainer was Muntz metal (an alloy of 60% copper, 40% zinc). To facilitate laboratory testing, special test specimens of the type suggested and prepared by the Eclipse-Pioneer Division of Bendix Aviation Corporation were employed. Each unit consisted of an optically polished disc of steel (SAE 52100) 1/8 inch thick and 1 inch in diameter, and a Muntz-metal specimen 1/2 inch wide, about 1-3/4 inch long, and 1/64 inch thick. A dimple was pressed in the center of the Muntz-metal component, which was then bent to form a clip so that the flat rim ringing the dimple would be held tightly against the polished surface of the steel (Figure 1). In conducting the tests, a drop of lubricant under study was placed on the steel disc; and the dimple part of the brass clip was positioned directly over the oil drop with the remainder of the brass specimen contacting the polished steel surface. In order to study the mechanism of corrosion, it was necessary to produce similar corrosion under laboratory conditions.

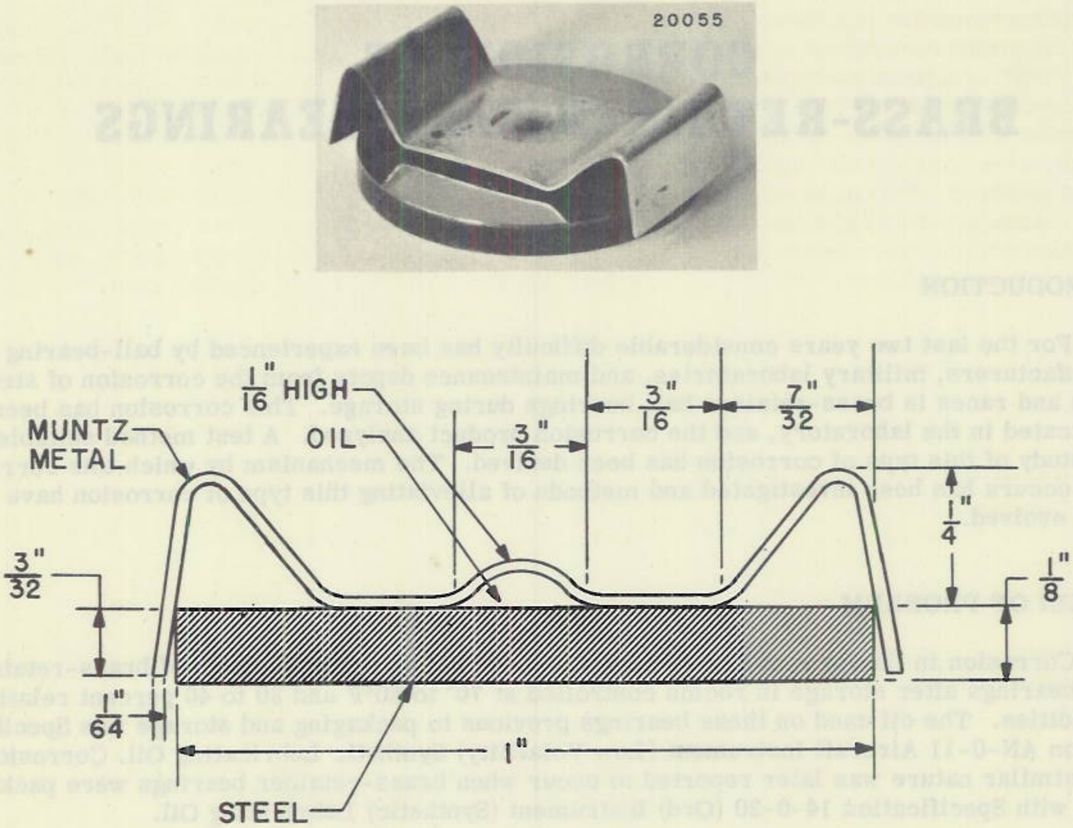

Figure 1 - Test specimen

Laboratory tests No. 1, 2, and 3 (Table 1) with carefully cleaned specimens indicated more stringent test conditions would be necessary to produce corrosion in a short time in the laboratory. Therefore, a lubricant was prepared using 16.6 percent by weight of barium mahogany sulfonate in di (2-ethylhexyl) sebacate. With this high concentration of rust inhibitor in diester, only slight corrosion occurred after exposure for 60 days at 77°F and 38-42 percent relative humidity (Table 1, test No. 4). In order to further increase the amount of corrosion produced under laboratory conditions, the specimens were exposed to temperatures of 136°F at a relative humidity of 36 percent. Under these conditions the steel specimen corroded at an accelerated rate (Table 1, tests No. 5, 6, 7, and 8). On test No. 5 slight corrosion had formed on the test specimens after 4 days exposure; test No. 6 was conducted under the same test conditions as test No. 5 but was exposed for 7 days and resulted in medium corrosion of the steel. The rate of corrosion diminished rapidly after 7 days exposure. In test No. 7, an additional drop of the inhibited oil was placed between the specimens after 7 days and the test was continued for 14 days, when medium heavy corrosion was observed on the steel specimens. Since the rate of corrosion also decreased after 14 days exposure on test No. 7, test No. 8 was conducted and additional drops of the inhibited oil were placed between the test specimens after 7 and 14 days. At the end of the test (21 days) heavy corrosion of the steel specimens was observed.

The deposit formed on the steel surface in the above tests could not be removed by organic solvents. The 18 steel specimens of test No. 8 were thoroughly washed in benzene and acetone in order to remove the excess lubricant and rust inhibitor. By scraping the corrosion product from the steel specimens with a new razor blade, care being taken not to scratch or abrade the steel surface, 0.197 mg of corrosion material was obtained. After ignition of this material at 800°C in a muffle furnace to constant weight, 0.151 mg was left, i.e., there was a loss of 0.046 mg. A qualitative spectrographic analysis of this corrosion material yielded mostly iron with traces of copper and zinc but was negative for barium. If the corrosion product before ignition is considered to be mostly $Fe(OH)_3$, then on ignition Fe_2O_3 is formed according to:

$$2\,Fe(OH)_3 \xrightarrow{\text{ignite}} Fe_2O_3 + 3\,H_2O$$

Theoretically 0.147 mg of Fe_2O_3 would be obtained from 0.197 mg of corrosion product; actually 0.151 mg was obtained. This deposit also contained traces of copper and zinc.

TABLE 1
Effect of Variations in Oils, Cleaning Procedures,
Temperature and Humidity on Corrosion of Steel-Brass Test Specimens

Test No.	No. of Specimens	Test Oil	Cleaning Procedure	Exposure Conditions			Results
				Temp. (°F)	Rel. Hum. (%)	Time (Days)	(Specimens Were Examined at 20 Magnifications)
1	6	AN-0-11	*	77	38-42	30	No rust during test period
2	6	AN-0-11	†	77	38-42	7	Rust of all specimens
3	6	AN-0-11	‡	77	38-42	30	No rust during test period
4	6	Di (2-ethylhexyl) sebacate + 16.6% by wt. of barium mahogany sulfonate (§)	‡	77	38-42	60	Small specks of brown deposit
5	6	Di (2-ethylhexyl) sebacate + 16.6% by wt. of barium mahogany sulfonate (§)	‡	136	36	4	Slight corrosion of steel
6	6	Di (2-ethylhexyl) sebacate + 16.6% by wt. of barium mahogany sulfonate (§)	‡	136	36	7	Medium corrosion of steel
7	6	Di (2-ethylhexyl) sebacate + 16.6% by wt. of barium mahogany sulfonate (§) (**)	‡	136	36	14	Medium heavy corrosion of steel
8	18	Di (2-ethylhexyl) sebacate + 16.6% by wt. of barium mahogany sulfonate (§) (††)	‡	136	36	21	Heavy corrosion of steel
9	2	AN-0-11	‡	136	0	30	No corrosion
10	2	14-0-20	‡	136	0	30	No corrosion
11	2	AN-0-6a	‡	136	0	30	No corrosion
12	2	Petroleum oil, grade 2135 + 1% by wt. of lauric acid	‡	136	0	30	No corrosion
13	2	Petroleum oil, grade 2135 + 1% by wt. of caproic acid	‡	136	0	30	No corrosion
14	2	Di (2-ethylhexyl) sebacate + 1% by wt. of lauric acid (§)	‡	136	0	30	No corrosion
15	2	Di (2-ethylhexyl) sebacate + 1% by wt. of caproic acid (§)	‡	136	0	30	No corrosion
16	2	Di (2-ethylhexyl) sebacate + 16.6% by wt. of barium mahogany sulfonate (§)	‡	136	0	30	No corrosion

* Cleaned by normal laboratory techniques

† Muntz-metal clips were cleaned in KOH and were not thoroughly rinsed

‡ Muntz-metal clips were cleaned as in (†) but were thoroughly rinsed and dried before being used.

§ Di (2-ethylhexyl) sebacate was inhibited with 0.25 percent 4-tertbutyl-4-phenylphenol as an oxidation inhibitor along with the rust inhibitor

** One extra drop of test oil was placed on each specimen after 7 days exposure

†† One extra drop of test oil was placed on each specimen after 7 days exposure and another drop after 14 days exposure

In order to observe the effect of humidity on the corrosion of brass in contact with steel, a series of tests were made in desiccators over anhydrous calcium chloride. None of the specification lubricants AN-0-11, 14-0-20, or AN-0-6a caused corrosion on a steel-brass couple in the absence of water vapor even at 136°F for 30 days (Table 1, tests No. 9, 10, and 11). It is also shown (Table 1, tests No. 12, 13, 14, and 15) that neither 2135 petroleum oil or di (2-ethylhexyl) sebacate, when inhibited with carboxylic acids, cause corrosion of steel in contact with brass in the absence of water under the same exposure conditions. It is further demonstrated (Table 1, test No. 16) that even the highly inhibited di (2-ethylhexyl) sebacate does not cause corrosion of the steel in the absence of water, whereas in the presence of a relative humidity of only 36 percent heavy corrosion was obtained (Table 1, test No. 8).

The galvanic action taking place between different metal couples in diester-type lubricants was studied by employing tests using a high concentration of barium mahogany sulfonate in di(2-ethylhexyl) sebacate at 136°F and 36 percent relative humidity. The results of these tests after 60 days exposure are given in Table 2. Test No. 17 shows that under these exposure conditions slight corrosion will take place between two pieces of steel (one SAE 52100, the other SAE 1020) placed in contact with each other with a drop of the inhibited diester between them. Test No. 18 clearly demonstrates the findings of Uhlig (1) that zinc may become cathodic to iron under certain conditions of exposure. Tests No. 19 through 28 give the results after 60 days exposure when a variety of metals were utilized to explore the galvanic action between different metal combinations.

TABLE 2

Effect of Variation in Second Component in Galvanic Test Specimens Using 16.6 Percent by Weight of Barium Mahogany Sulfonate in Di (2-ethylhexyl) Sebacate at 136°F and 36 Percent Relative Humidity (specimens examined at 20 magnification)

Test No.	Type of Specimen	No. of Specimens	Results after Exposure for 60 Days
17	Steel on steel	2	Corrosion of both specimens
18	Zinc on steel	2	Corrosion of steel only
19	Copper on steel	2	Very slight corrosion of steel, slight discoloration of copper
20	Copper on zinc	2	Tarnish of copper
21	Muntz metal on silver	2	Tarnish of silver
22	Muntz metal on tin	2	Very slight discoloration of tin
23	Muntz metal on cadmium	2	No corrosion of either
24	Muntz metal on aluminum	2	No corrosion of either
25	Muntz metal on lead	2	Very slight discoloration of lead
26	Muntz metal on glass	2	No discoloration of either
27	Muntz metal on steel	2	Corrosion of steel
28	Muntz metal on nickel	2	No corrosion of either

To discover if corrosion occurred on steel coupled to brass at 136°F and 36 percent relative humidity in the presence of uninhibited lubricants, tests were made (Table 3, No. 29 and 30) which showed that after 60 days exposure corrosion had occurred when both di (2-ethylhexyl) sebacate and grade 2135 petroleum oil were used. Somewhat greater corrosion occurred on the steel specimens when AN-0-11 and AN-0-6a specification lubricants were used (tests No. 31 and 32). These tests demonstrate that additives are not essential to this type of corrosion but that they undoubtedly contribute to the rate of corrosion on steel-brass couples in the presence of these lubricants.

Synthetic lubricants corresponding to Ordnance Specification 14-0-20 were not investigated further because it was thought that their performance would be closely allied to that of the AN-0-11 specification lubricant.

Realizing that the corrosion encountered in these tests is electrolytic in nature and is probably accelerated by small quantities of acids which were formed by oxidation or hydrolysis of the lubricant, it was now necessary to develop methods or lubricating compositions which could be used to alleviate this corrosion. Of the compositions evaluated and reported in Table 4, test No. 41, in which 1.0 percent of cetyldimethylamine was used in di (2-ethylhexyl) sebacate, is interesting. Although this composition gave no corrosion on the steel discs after 60 days exposure at 136°F and 36 percent relative humidity, the amine is not an efficient inhibitor at higher relative humidities. It does, however, have the ability to combine with small amounts of acids that may be formed during the exposure period, thus rendering them incapable of promoting electrolytic corrosion. Also, in test No. 46 the amine alone, when added to the highly rust inhibited diester, was effective in eliminating the electrolytic corrosion involving the steel specimen.

TABLE 3
Effect of Omitting Rust Inhibitors
at 136°F and 36 Percent Relative Humidity
(specimens examined at 20 magnifications)

Test No.	Test Oil	No. of Specimens	Results after Exposure for	
			30 days	60 days
29	Uninhibited di (2-ethylhexyl) sebacate	2	No corrosion	Medium corrosion of steel
30	Uninhibited grade 2135 petroleum oil	2	No corrosion	Medium corrosion of steel
31	AN-0-11 spec. synthetic lubricant	2	Slight corrosion of steel	Medium corrosion of steel
32	AN-0-6a spec. petroleum lubricant	2	Slight corrosion of steel	Medium corrosion of steel

TABLE 4
Effect of Various Rust Inhibitors
When Used 1 Percent by Weight in Oxidation Inhibited*
Di (2-ethylhexyl) Sebacate at 136°F and 36 Percent Relative Humidity

Test No.	Rust Inhibitor	No. of Specimens	Results after Exposure for 60 Days
33	Barium mahogany sulfonate (14-0-20 Ord Spec.)	2	Dendritic type of deposit
34	Zinc naphthenate	2	Few brown corrosion specks
35	Barium mahogany sulfonate	2	Dendritic type deposit
36	Sorbitan monooleate	2	Few brown corrosion specks
37	Barium naphthenate	2	Dendritic type deposit
38	Glyceryl oleate	2	Several tan corrosion spots
39	Cetyldimethylammonium phenylstearate	2	No deposit
40	Blank - diester only	2	Faint dendritic corrosion
41	Cetyldimethylamine	2	No corrosion on steel, brass slightly tarnished
42	Cetyldimethylammonium naphthenate	4	No corrosion on steel, brass slightly tarnished
43	Cetyldimethylammonium octodecylbenzenesulfonate	4	No corrosion on steel, brass slightly tarnished
44	AN-0-11 spec., synthetic lubricant, with the addition of 1 percent by weight cetyldimethylammonium phenylstearate	4	No corrosion on steel, brass slightly tarnished
45	AN-0-6a spec., petroleum oil with the addition of 1 percent by weight of myristyldimethylammonium phenylstearate	4	No corrosion on steel, brass slightly tarnished
46	16.6 percent by weight of barium mahogany sulfonate and 1 percent by weight of cetyldimethylamine in di (2-ethylhexyl) sebacate	4	No corrosion on steel, but brass was dark tan in color

*Oxidation inhibitor was 0.25 percent by weight of 4-tertbutyl-4-phenylphenol

By combining the acid neutralizing qualities of an amine with the rust inhibiting qualities of an acid and developing amine-acid complexes we have the rust inhibitors used in tests No. 42, 43, 44, 45 (Table 4). Previous work at this Laboratory (2) has demonstrated that cetyldimethylamine has the property of reacting reversibly with 2 or 4 moles of acid. As the compositions used consisted of equal moles of the tertiary amine and the organic acid, the former could be expected to combine with and render inactive a further appreciable quantity of acid. In addition to their acid-neutralizing ability these compositions possess excellent rust inhibition properties (3), (4), (5). Both tests No. 42 and 43 (Table 4) pass the 168 hour static water-drop corrosion test (4) at 140°F with distilled water.

DISCUSSION

It should be pointed out that the corrosion deposit always formed on the steel specimens; the brass specimens were slightly discolored but free from deposit. For the purpose of analysis the corrosion deposit was scraped from the steel specimens only; therefore, the copper and zinc found on analysis must have been transferred from the Muntz metal to the corrosion deposit on the steel surface by some form of chemical reaction. The nonferrous metals may have been present in the corrosion products as insoluble metal salts or as free metal deposited by a displacement reaction with the iron. Wilkins and Jenks (6) state that copper coupled with iron and zinc has a tendency to accelerate attack on these metals when exposed to mildly corrosive types of aqueous solutions such as rain water or other fresh water, dilute salt solutions, and moist atmospheres. Galvanized steel or iron has been subject to failure as a consequence of couples involving copper. Anderson and Reinhard (7) state that zinc may be used safely in contact with many organic liquids provided they are nearly neutral in pH and are substantially free from water. Uhlig (1) states that the corrosion of iron is retarded in most aqueous media when iron is coupled with zinc, but zinc may actually become cathodic to iron in fresh water at slightly elevated temperatures. The above would indicate that under certain conditions peculiar behavior could be expected between the Muntz metal and steel.

As the rust inhibitor used is barium mahogany sulfonate, the absence of barium in the corrosion product indicates that precipitation of the rust inhibitor itself is not responsible for the deposits obtained. It is still possible that the rust inhibitor might be a source for an acid which would serve to accelerate the rate of corrosion between the Muntz metal and steel specimens. As barium mahogany sulfonate consists of a strong acid and a strong base, hydrolysis to give sulfonic acids is improbable. However, many petroleum sulfonates contain about 5 percent carboxylic acids whose barium salts would be easily hydrolyzed to give carboxylic acids in the presence of small quantities of water.

The effectiveness of cetyldimethylamine in reducing the incidence of corrosion in these steel-brass systems suggests strongly that acids are an important factor in the corrosion process. Small quantities of acids could have been formed by hydrolysis of di(2-ethylhexyl) sebacate present as the vehicle or lubricant in AN-0-11 and 14-0-20 synthetic fluids and from the rust inhibitor present in the AN-0-11, 14-0-20, and the AN-0-6a specifications. Small quantities of corrosive acids could also be formed by oxidation of the petroleum oil which is the vehicle and lubricant of AN-0-6a. The diesters are not as stable towards hydrolysis as are petroleum oils, but the oxidation stability of diesters exceeds that of petroleum oils (8). Water is also more soluble in the diesters than in petroleum oils, and so may pass through the oil phase of the former to hygroscopic corrosion points more rapidly. In rust inhibited petroleum oils, carboxylic acids could be formed by oxidation or by hydrolysis of metal naphthenates or from polyhydroxy esters of carboxylic acids which are frequently used as rust inhibitors. Any inhibitor or lubricant that would deteriorate to give even small quantities of low molecular weight acids would give trouble when used to inhibit or lubricate steel in contact with brass.

As the whole problem of brass-retainer ball bearing corrosion is influenced by carboxylic acids and water and as any kind of oil, synthetic or petroleum will eventually generate carboxylic acids by the process of oxidation or hydrolysis, it would be better to eliminate the use of brass retainers.

The following facts have been established up to this point:

1. The corrosion experienced with brass-retainer (Muntz-metal) ball bearings lubricated with AN-0-11 synthetic lubricant is galvanic in nature, the corrosion product being iron rust.

2. Water is essential to the corrosion process.

3. The presence of the iron-brass couple gives approximately a ten-fold greater rate of corrosion than an iron-iron couple.

4. Copper alone is inactive. Zinc alone is very active, but not more active than brass.

5. The presence of commercial alkaline earth mahogany sulfonates increases corrosion under the conditions described although barium compounds do not appear in the corrosion deposit.

6. Traces of potassium hydroxide left from cleaning the brass accelerate the normal galvanic action by about eight-fold.

7. Corrosion at low humidities is more pronounced in the presence of a diester type oil than with a petroleum oil containing the same rust inhibitor.

8. Cetyldimethylamine is a powerful inhibitor of galvanic corrosion, even in the presence of a high concentration of barium mahogany sulfonate (16.6 percent). A still stronger inhibitory effect is shown by (a) cetyldimethylammonium stearate, (b) cetyldimethylammonium naphthenate, (c) cetyldimethylammonium octadecylbenzene sulfonate.

An explanation of corrosion of the type just discussed can now be advanced, and is briefly as follows:

1. Galvanic corrosion in brass-retainer ball bearings at low relative humidities occurs only in the presence of a conducting film or path of water between the two unlike metals.

2. The galvanic couple may be formed by contact of the original dissimilar metal components, or by the displacement deposition of copper or zinc metal from compounds formed by the attack of organic acids on the brass component. This deposition would be expected to occur from droplets of hygroscopic electrolyte solution in contact with the steel. Such secondary couples would be formed most frequently near the point of contact with the brass but could occasionally occur at more distant points.

3. Such a film can exist at 36 percent relative humidity only in the presence of hygroscopic or extremely water-soluble compounds. Such films might result from: (a) the formation of water-soluble salts of zinc or copper by the action of oxygen and organic acids; (b) traces of potassium hydroxide or other water soluble contaminants from the cleaning solution; (c) hygroscopic impurities in the alkali or alkaline earth sulfonates used as inhibitors; (d) hydrolysis of carboxylate salts (present in small amounts even in mahogany sulfonates) at oil-water interface to give an electrolyte-metal compound in water and an oil soluble organic acid; and (e) hydrolysis of diester to give water-soluble sebacic acid or metal sebacates.

4. The deposit of corrosion products is porous and supplies a path in which concentrated water solution may extend the electrolytic action to new metal at the boundary of the corroded area.

5. Cetyldimethylamine inhibits the type of corrosion under consideration (a) by neutralizing water-soluble acids and holding them in the oil phase, thus reducing the conductance and hygroscopicity of any aqueous phase present; (b) by forming oil-soluble complexes with zinc or copper ions already present and removing them from the water phase where they act as electrolytes; (c) possibly by cooperative adsorption with inhibitor acids at the metal surface, in such a way as to give a more firmly adsorbed film with better resistance to penetration by micro drops of hygroscopic salt solutions, such as may be present in the sulfonate oil system.

Care must be taken in using the amine-acid complexes as inhibitors for the following reasons (9):

1. If too much acid should be generated, the capacity of the amine to remove acid would soon be satisfied; then corrosion would proceed as usual.

2. Amines might be corrosive to brass in the systems; however, high molecular weight amines, especially the tertiary amines without the active hydrogen, are less corrosive to copper than are some of the low molecular weight amines (3).

3. If the lubricants are to perform at high temperatures, care must be taken that the temperature does not exceed that at which decomposition of the additives would take place. For high-temperature performance, metal deactivators or more heat stable neutralizers for acids deserve study. Moving parts would be a problem if metal deactivators were being considered.

CONCLUSIONS

It is concluded that:

1. The corrosion observed at low relative humidities with brass-retainer ball bearings when lubricated with AN-0-11 synthetic lubricant is galvanic in nature. Water must be present, and the corrosion product is iron rust. The same phenomenon in less acute form is observed in the presence of rust-inhibited petroleum oils.

2. The corrosion process is accelerated by (a) the presence of rust inhibitors, such as barium mahogany sulfonate; (b) residual electrolytes from the cleaning process; (c) small amounts of organic acids resulting from the oxidation of the lubricant, from the hydrolysis of the ester type base oil, or from the hydrolysis of the small quantities of metal carboxylates found in most petroleum sulfonates.

3. This corrosion can be prevented or greatly reduced by the use of corrosion inhibitors capable of neutralizing acids as they are formed. Inhibitors that have been found useful include high molecular weight tertiary amines and their complexes with oil soluble organic acids of high molecular weight, e.g., cetyldimethylammonium stearate.

4. Since this corrosion at low humidities has been found serious only in the presence of brass, it appears that the use of this material for separators in ball bearings should be discouraged, and that the separators should be fabricated from steel, a plastic, or nonferrous metal or alloy less susceptible to chemical attack.

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