DIESEL ENGINE COOLANT INVESTIGATIONS

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An account is given of the development of a laboratory coolant test rig for the evaluation of corrosion inhibitors for both water and antifreeze diesel engine coolants. This paper also comments on the rig operating experience gained so far and reports on the variety of coolant problems investigated with the test rig.

It is emphasized that laboratory corrosion studies can only give meaningful results if they ensure that experiments take reasonable account of all factors likely to affect corrosion under service conditions. These factors are itemized together with their likely effects on corrosion. Attention is also drawn to the fact that inhibitors must not have an adverse effect on heat transfer, even if they effectively prevent metals corroding.

Details of a number of engine tests are given and comparison of engine and rig inhibitor depletion rates can be made to verify the validity of the rig test procedure. An unusual experience is quoted to illustrate the importance of cleanliness in an engine's cooling system prior to the introduction of coolant.

Introduction

Severe damage to an engine cooling system component is rarely directly caused by loss of metal due to corrosion. On the other hand it is known that corrosion products can form thermal barriers on heat transfer surfaces, or restrict coolant flow, which lead to overheating and even to the cracking of cylinder heads. It is therefore customary to add corrosion inhibitors to engine coolants in order to prevent these undesirable effects. In considering diesel engines, Barton (1), Keerabhadra Rao (2) and others have shown that the use of appropriate inhibitors in the coolant can usefully reduce cavitation erosion attack on the water-side of cylinder liners.

Type testing of a wide variety of marine diesels with powers ranging from 15 to 2000 kW is undertaken at the Admiralty Engineering Laboratory (AEL). Apparently this provides a means of comparing the effectiveness of different inhibitor formulations under true working conditions. Unfortunately, this can be an extremely lengthy procedure as a minimum of 1000 hours' running is required for an appreciation of inhibitor performance. In the engine test programmes, the evaluation of corrosion inhibitors is of secondary importance so that it is virtually impossible to obtain valid comparisons resulting from variations in frequency, time and conditions of running of any of the engines available. It became apparent that a laboratory test was required that compared engine coolant inhibitors realistically in as short a time as possible. The attractions of this approach were the ability to exercise laboratory control, the use of comparatively small quantities of inhibitor, the elimination of possible damage to an expensive engine by ineffective treatment, and the available accumulation of data from engine tests on established formulations to compare with laboratory test results.

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Other organizations, such as chemical and engine manufacturers, and research associations had seen this need, and a variety of test procedures were found to be in operation (3–6). Indeed, the first AEL coolant test rig was based on one developed by Collins and Glover (6) which gave results that encouraged this approach to the problem. The methods used included simple glassware screening tests, metal specimens being revolved at high speeds in inhibited solutions, and circulating rigs containing actual engine components. It almost seemed as if there was a tacit agreement that no two test methods should be alike.

It was patently obvious that the time was ripe for interested parties to get together and agree on test methods. Fortunately, at this time, a number of inhibited antifreeze formulations were being submitted to the British Standards Institute for approval; some of these were claimed to be superior to the three existing compositional standards BS 3150, 3151 and 3152 (1959). The BSI therefore decided to set up Panel CIC/7/–/2 to recommend performance tests for antifreeze on which the MOD was represented by a member of AEL's staff.

The recommendations of this panel are due to be published shortly and will describe four types of test:

(1) a simple glassware sorting test;

(2) a laboratory recirculating rig test;

(3) static engine tests;

(4) tests on engines in service.

Although the members of this panel were mainly drawn from the car and chemical industries, the rig test was seen to be well suited for reproducing the running conditions of marine diesel engines. Consequently, four rigs based on these recommendations are currently in use at the AEL.

Factors Affecting Corrosion of Cooling Systems

Corrosion can be defined as the gradual loss of usefulness of a metal as it slowly reverts to its natural state because of chemical or electro-chemical reaction with its environment. At a first glance it would seem that the inhibitors for a particular system should be selected solely according to the materials of construction. However, there are a number of factors which can influence their performance and which have to be considered when devising a laboratory test that can be adapted to simulate a particular system. These major variables and their possible effects are:

(a) Variety of alloys present—Varying inhibitor effectiveness and demand, possible creation of undesirable galvanic couples;

(b) Metal surface condition—Rough surfaces, especially those already corroded, can have a very high inhibitor demand;

(c) Metal surface temperature—Affects nature of corrosion products and could affect stability of inhibitors;

(d) System design—Localized attack in crevices or due to turbulence. Ratio of metal surface area to coolant volume determines inhibitor demand;

(e) Water composition—Impurities, particularly chlorides and sulphates, can aggravate corrosion, whereas carbonates could form protective skins;

(f) Degree of aeration—Oxygen is a cathodic depolarizer and anodic passivator. Some inhibitors are much more effective in the presence of dissolved oxygen (7);

(g) Inhibitor concentration—Insufficient anodic inhibitors such as chromates can lead to highly localized aggressive corrosion at unprotected sites;

(h) Coolant flowrate—Affects removal of corrosion products and supply of inhibitor to metal surfaces;

(i) Coolant temperature—Affects solubility of corrosion products and rate of corrosion reactions;

(j) Thermal cycling—Differences between the expansion coefficients of metals and their corrosion products can cause breakaway of surface layers exposing more metal for protection;

(k) Vibration—In severe cases this causes cavitation erosion but also affects access of oxygen to cathodic sites and transport of metal ions from anodic sites (8);

(l) pH of coolant—Most inhibitors are only effective over a limited pH range;

(m) Exhaust gas leakage—Lowering of coolant's pH due to formation of carbonic, sulphurous and sulphuric acids.

The MOD has a specific additional interest in the performance of inhibited coolants under prolonged cold idle conditions and it is surprising that some well established formulations give poor protection when thus used. Howard (9) has made cold glassware tests with both deionized and aggressive water solutions of the three BSI inhibited antifreeze formulations. These have shown that in some such cases corrosion can be almost as severe as in solutions maintained at 90°C, and with one solution the corrosion of solder was much greater in the cold than in the hot test. Indeed, much work has been done in the United States to find suitable container materials for an inhibited glycol, as the intended formulation severely corroded tinplate within three months standing.

Rig Outline

The design and operating conditions of the rig, which will eventually be described in detail in a BSI publication, is of necessity a compromise. In particular, a surprisingly large difference exists in the ratio of coolant volume to wetted metal surface area for different types of engine. It is not anticipated, however, that running experience will indicate the need for any major modifications, though some changes could be made when investigating specific problems.

Fig. 1 illustrates the layout of the rig which consists of a reservoir, head tank, pump and connecting pipework which are supported on a mild steel frame. The assembly is 105 cm high and occupies a bench space no larger than 60 × 30 cm. The recirculating coolant under test is heated by two electric cartridge heaters inserted into metal sheaths in the reservoir; the temperature is thermostatically controlled. A 'cold finger' condenser is sited in the head tank for cooling and into this tank lid is fitted an air inlet for aeration of the coolant to accelerate corrosion. The incorporation of a relief valve allows for controlled pressurization of the system. Four sets of metal corrosion test coupons are mounted in the pipework and two sets are placed in the reservoir. Owing to the large inhibitor demand of solder on some formulations, a coil of solder is placed in the head tank when testing inhibitors for car cooling systems.

Rig Components

Reservoir

The reservoir is a machined casting of the predominant alloy in the cooling system of interest, which is usually cast iron or aluminium. It is a flanged
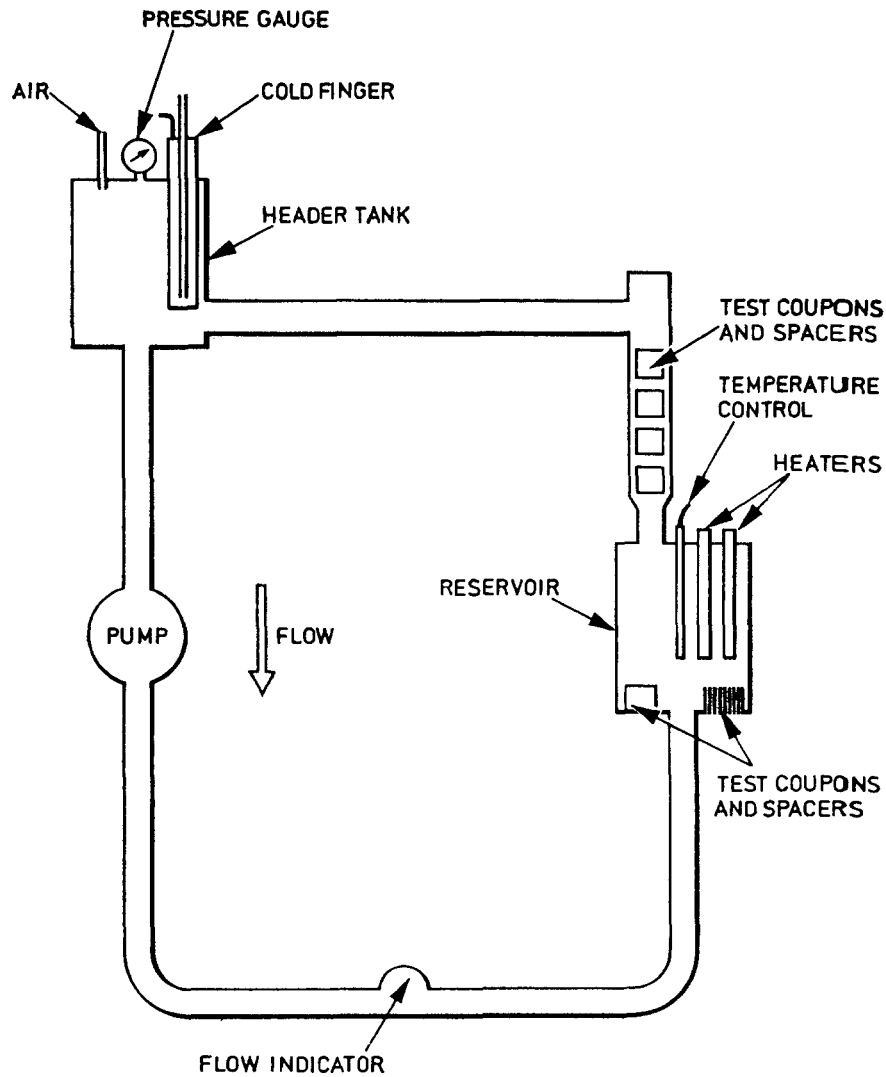
Fig. 1—Layout of coolant test rig

cylinder with an inlet pipe in its base. A lid is bolted to the flange and seated on a rubber O-ring to form a seal. Into the lid are fitted the exit pipe, a thermostat bulb and the sheathed cartridge heaters.

Heaters and Sheaths

The two cartridge heaters are so arranged that one of them runs continuously whilst the other operates intermittently under thermostatic control to maintain a steady solution temperature. Each heater is inserted into a metal sheath and a little silicone fluid added to aid heat transfer. The sheath is made of whatever alloy is likely to be the hottest in the engine system under consideration and, if required, can be fitted with thermocouples for temperature measurements.

Head Tank

The head tank is of brass and has similar dimensions and lid sealing arrangements to the reservoir. The liquid inlet is a sidearm, and the exit is a tube in the base. In the lid is fitted a copper air inlet tube, relief valve and pressure gauge. An air filter-regulator and flowmeter are, of course, incorporated in the air feed.

Cold Finger

The 'cold finger' is a copper cylinder, sealed at both ends, which is secured to the lid of the head tank by a clamp plate.

Cold water inlet and outlet points are at the same end, with the inlet tube extending almost to the other end of the cylinder. Water flow is maintained at a sufficient rate for the exit temperature to be below 35°C.

Pump

The pump is glandless and centrifugal. Before starting a test it is calibrated to give a flow rate of 10 ± 1 litre/min. at 95°C. This is achieved by inserting a flow-meter in the system in place of the specimen hose.

Pipework

The connecting pipework, which is renewed for each test, is made of heat and pressure-resistant rubber and, as shown in Fig. 1, includes a flow indicator mounted horizontally below the pump. The section of pipework above the reservoir is of wide-bore rubber to accommodate the metal test coupons.

Metal Test Specimens

Metal specimens are all prepared with a central hole and the customary precautions taken to ensure that each specimen has a uniform surface finish before they are cleaned, dried and then weighed to the nearest milligramme. A typical assembly of six alloys would include aluminium, cast iron, mild steel, brass, solder and copper.
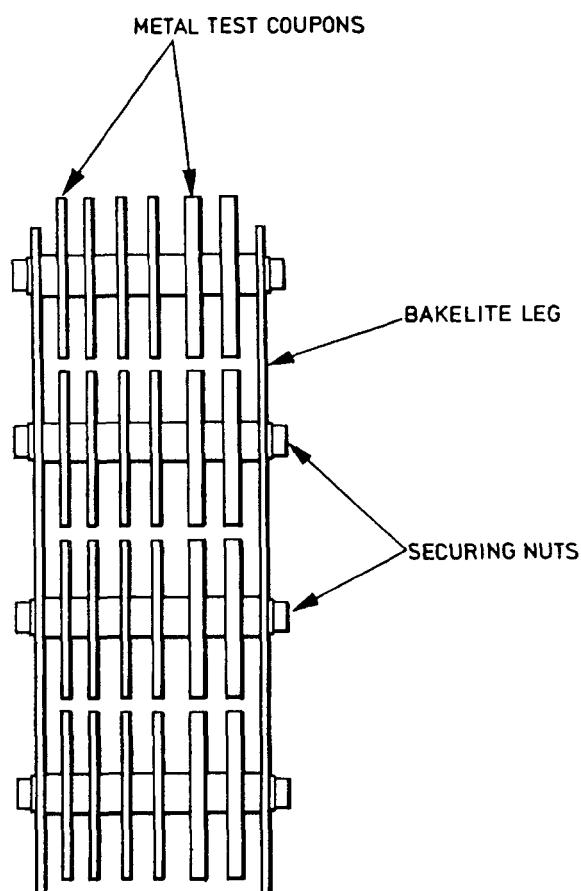

FIG. 2—TEST SPECIMEN ASSEMBLY

The specimens are assembled on a plastic-sleeved brass rod that passes through the central hole of each one. They are separated by cylindrical spacers, the material of which can be selected to give either electrical contact or insulation between adjacent alloys. At each end of the two assemblies for the reservoir is placed a bakelite 'leg' and they are all tightened together by a nut at each end of the rod to ensure good contact between specimens and their adjacent spacers. FIG. 2 shows the similar arrangement of the four specimen sets placed in the hose, where it will be seen that the two elongated 'legs' separate the sets from each other but hold them in line to reduce turbulence.

In the BSI publication details will be given of the dimension and materials of construction of the reservoir, head tank, test specimen alloys and spacers. The order of assembly of the test specimens will also be specified together with procedures for their surface preparation and post-test cleaning.

Test Procedure

A standard volume of the inhibited coolant to be tested is introduced into the rig at the head tank. The pump is started and aeration commenced at 10 ± 0.5 ml/min. with the pressure being set at 700 ± 7 mb. This is followed by the heaters being switched on to raise the temperature of the circulating coolant to $95 \pm 2°C$, at which point the cooling water supply to the cold finger is commenced.

A test lasts for six weeks and includes a number of shut-down periods which are planned so that the rig is run for a total of 774 hours and idle for 234 hours. Each week includes a 72-hour continuous run, a 24-hour shut-down period and three separate 5-hour shut-down periods. These idle periods are commenced by simultaneously switching off the heaters and pump, but maintaining the cold finger cooling water supply until the test solution is at room temperature. Losses due to leakage or evaporation are made good with distilled water during idle periods, but a test is invalidated if the total amount of these additions exceeds 500 ml.

At the end of the test, the rig is dismantled and the metal specimens removed, cleaned, dried and reweighed to determine weight losses. Tenacious corrosion products, which could cause an apparent increase in weight, are removed by the appropriate chemical treatment. All other rig components are visually inspected, particularly the heater sheaths which can be used as valuable extra corrosion test specimens. Additional useful information can also be obtained by analysing the coolant for inhibitor concentration before and after the test, and small samples can be taken periodically for pH monitoring.

Objectives of Rig Testing

The coolant test rigs at AEL are being applied to the following principal objectives:

(*i*) collaborating with other rig operators in conducting similar tests, using the same range of alloys on 25 per cent. aqueous solutions of BS 3150 and BS 3151 inhibited ethylene glycol. These solutions were all prepared with agreed concentrations of sodium salts to produce a standard aggressive water containing chloride, sulphate and bicarbonate ions;

(*ii*) comparing various corrosion inhibitor formulations in 20 per cent. aqueous solutions of ethylene glycol. These solutions were prepared with distilled water as used in ships of the Royal Navy; a solder coil was not placed in the head tank, as was the case in objective (1);

(*iii*) comparing the effectiveness of a limited range of proprietary inhibitor formulations in distilled water using either cast iron or LM8 aluminium alloy reservoirs. The range was not extended as one formulation showed such promise that it is being more thoroughly investigated;

(*iv*) determination of the effects of the environmental conditions of an engine cooling system upon certain additives to antifreeze solutions. These additives are being considered as a means of detecting glycol leakage into the engine's lubricating oil;

(*v*) investigating a report that Kanigen (a high phosphorus nickel alloy) plated cast iron cylinder heads are adversely affected by the formation of a thermal insulating deposit when cooled with phosphate inhibited antifreeze.

Inhibited Ethylene Glycols

Regard for commercial interests prohibits the detailing of inhibitors and their concentrations in proprietary formulations. However, these can be given

for the three British Standards for ethylene glycol as used in antifreeze soluti ons:

BS 3150. 0·2–0·3 per cent. NaMBT (sodium mercaptobenzothiazole) and 0·9–1·0 per cent. phosphoric acid with triethanolamine added to adjust pH;

BS 3151. 0·55 per cent. sodium nitrite and 7·5 per cent. sodium benzoate;

BS 3152. 2·4–3·0 per cent. sodium tetraborate.

Rig Operating Experience

Objective 1

Owing to the pressure of other commitments, the AEL has been unable to contribute as much as had been hoped to the collaborative tests. Nevertheless, operating experience gained in other 'non-standard' work has assisted in deliberations on how to tighten up procedures with the object of obtaining more reproducible results.

Investigators unfamiliar with corrosion testing data were possibly disappointed by the spread of results obtained from the first series of tests. However, comparison of the average weight losses of 10 tests on BS 3150 and 12 tests on BS 3151 confirm the most popular belief that BS 3151 is the preferred formulation (Table I). It shows the effectiveness of NaMBT, the specific inhibitor for copper base alloys in BS 3150 which is used extensively by the MOD. The breakdown of the BS 3150 glycol was demonstrated by the fact that 8 out of the 10 tests produced acid solutions on completion and 7 of these had to be prematurely terminated in order to protect the pump from circulating corrosion products.

Table I—*Metal specimen weight losses in inhibited 25 per cent. solutions of ethylene glycol in standard 'aggressive' water. Cast iron reservoir*

Formulation	BS 3150	BS 3151	BS 3152	'X'	Inhibitor 'A'
Number of tests	10	12	1	9	1
	Average weight loss (mg)				
Aluminium	112	27	83	103	38
Cast Iron	793	347	910	316	188
Mild Steel	482	60	419	137	149
Brass	9	45	4	21	47
Solder	294	47	12	133	66
Copper	10	184	9	24	2

Table I also shows the average specimen weight losses from 9 tests on a proprietary formulation 'X' and single test results on BS 3152 and on an ethylene glycol solution treated with inhibitor 'A', a formulation primarily intended for fresh-water coolants.

Visual inspection of the test coupons often showed that when weight losses were high, particularly for cast iron, pitting corrosion had occurred close to their central holes, i.e. on that part of their surfaces adjacent to a spacer. Weight losses of the heater sheaths have not been recorded although the same aluminium alloy was used in all tests quoted. On all of the BS 3150 tests, and
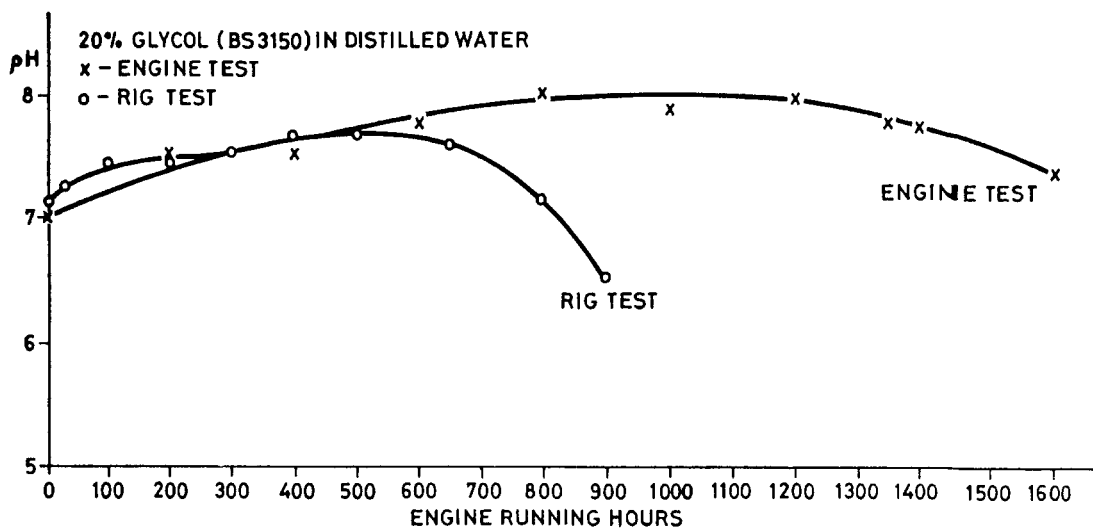
FIG. 3—TYPICAL ENGINE AND RIG TEST pH CHANGES WITH RUNNING TIME

some of the others, it was impossible to remove the baked-on deposits accurately to obtain a true weight loss. In general, where attack was visible, or a deposit had formed, the control heater sheath was less seriously affected than the one in continuous use.

Periodic checks of the pH and inhibitor concentrations of the test solutions showed trends similar to those observed in practice. The accelerated nature of the test was emphasized by a relatively early drop of pH to below 7 for many of the test runs. FIG. 3 compares a typical test rig result for the BS 3150 formulation with that obtained from a 16-cylinder engine with a cast iron cylinder head. Although, in some cases, moderate corrosion occurred with solutions which remained slighly alkaline, it was often possible to detect a change to acid conditions by the increase of circulating corrosion products visible in the flow indicator.

Collaborative work is continuing on shorter than standard tests with the aim of tightening up procedures to obtain closer inter-laboratory agreement. The areas of particular interest are metal specimen cleaning, solder coil location, maintenance of correct volume and flow rate, degree of aeration and the possible effect of different hose materials. However, the author considers that reasonable reproducibility of results will only be obtained with good inhibitor formulations that can withstand the test conditions, and that the most difficult factor to finally determine is the actual duration of the test.

Objective 2

When engines in vessels of the Royal Navy require antifreeze coolants it is customary to employ 20 per cent. aqueous solutions of inhibited ethylene glycol which have sufficiently low freezing points of approximately $-8°C$. Inhibited ethylene glycol can be purchased, thus governing the inhibitor concentration in prepared solutions. It was therefore considered necessary to use the rigs under typical service conditions where inhibitor concentrations are lower than in the previously described tests. All solutions were prepared with distilled water to further simulate normal practice.

TABLE II records the results obtained, with the non-standard formulations being the same as those previously tested. Inhibitor 'A' only was used at the same concentration as before because it has to be added to the antifreeze coolant prepared to the desired strength; it is not sufficiently soluble in undiluted ethylene glycol.

Further testing of these 20 per cent. glycol solutions was not considered necessary as the lower inhibitor concentrations apparently had no adverse effects for the duration of the tests. The use of an aggressive water and the inclusion of a coil of solder in the head tank required for the British Stand ard test seems to create a somewhat more severe condition.

It is interesting to note that no aeration was employed for the cast iron reservoir test on Inhibitor 'A'. No appreciable change in corrosion was noted other than a marked increase in that of solder. Similar experiences have been reported by other rig operators but for general comparisons the degree of aeration employed is preferred as it swamps accidental air ingress thus giving more reproducible test conditions.

One pleasing feature of these tests was the observed different depletion rates of NaMBT in BS 3150 according to the reservoir material. As shown in Fig. 4, depletion was less rapid with aluminium than with cast iron. This was in accord with engine operating experience and suggests that iron catalyzes the breakdown of this inhibitor or that NaMBT combines with ferrous alloys as well as the copper base alloys that it is intended to protect.

Table II—*Metal specimen weight losses in inhibited 20 per cent. solutions of ethylene glycol in distilled water*

Formulation	BS 3150		BS 3151		'X'		Inhibitor 'A'	
Number of tests	3	1	1	1	1	1	1	2
Reservoir	Iron	LM8	Iron	LM8	Iron	LM8	Iron	LM8
	Average weight loss (mg)							
Aluminium	48	47	42	24	54	36	47	25
Cast iron	554	525	491	575	298	248	197	298
Mild steel	300	370	332	235	236	131	206	136
Brass	6	5	29	15	4	18	24	16
Solder	148	134	30	6	32	23	97	26
Copper	4	1	57	111	2	6	5	7

20 % GLYCOL (BS 3150) IN DISTILLED WATER
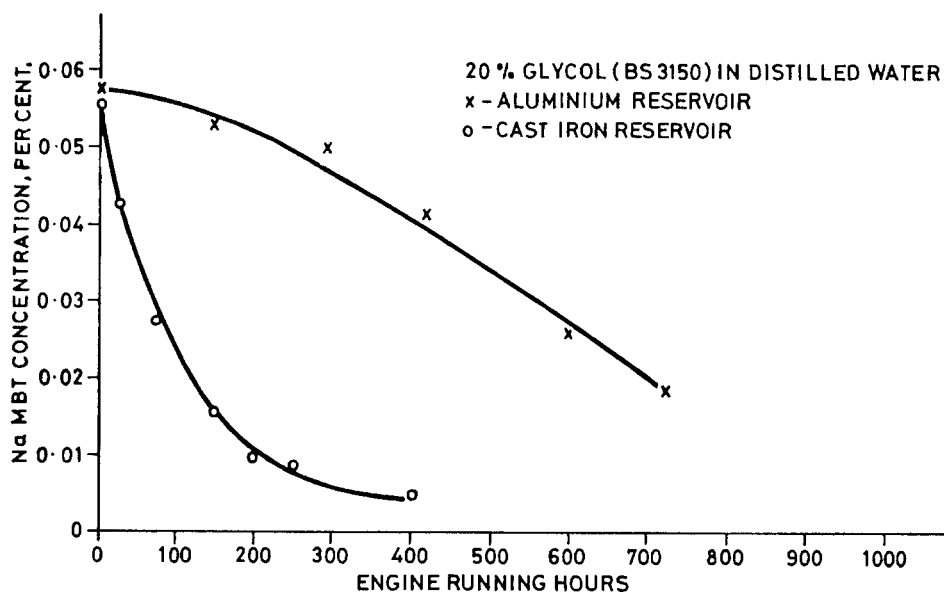x – ALUMINIUM RESERVOIR
o – CAST IRON RESERVOIR

Fig. 4—Depletion rates of NaMBT with alternative reservoir materials

TABLE III—*Metal specimen weight losses in inhibited distilled water*

Formulation	Inhibitor 'A'				Inhibitor 'B'	Inhibitor 'C'
Number of tests	3	1	1	1	3	3
Duration	6 wks	6 wks	3 wks	3 wks	3–5 wks	6 wks
Reservoir	Iron	LM8	Iron	Iron	Iron	Iron
Additions	—	—	1% SW	5% SW	—	—
Average weight loss (mg)						
Aluminium	3	20	16	32	71	172
Cast iron	18	67	210	447	580	13
Mild steel	14	75	121	237	8	6
Brass	2	7	5	22	27	19
Solder	23	31	32	36	93	127
Copper	2	3	4	4	33	33

Objective 3

Tests on various inhibitors in distilled water have given much better reproducibility of results, especially with the more effective formulations. TABLE III lists the results from rig testing three proprietary formulations and includes results from the best of these deliberately contaminated with seawater (SW).

Inhibitor 'A' was a liquid concentrate known to include sodium nitrite, silicate and tetraborate; inhibitor 'B' was a soluble oil; and inhibitor 'C' was a powder in which sodium salts, including nitrite, were blended.
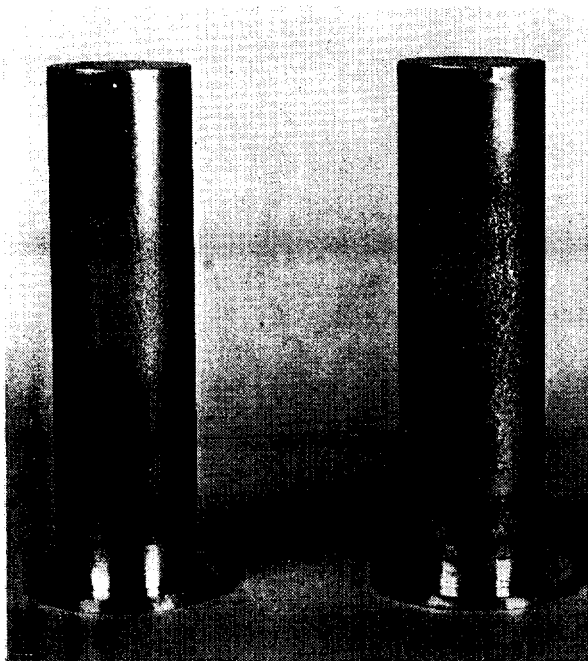

FIG. 5—PITTED ALUMINIUM HEATER SHEATHS

The range of inhibitors tested has not been extended as inhibitor 'A' justified more detailed examination, e.g. as to how it was affected by seawater contamination and its suitability as an additive for antifreeze solutions. Engine tests with this inhibitor and examination of cooling system components, such as cylinder liners, have confirmed its good performance. The seawater contamination tests were limited to three weeks' duration as it was hoped that contamination of this order would be detected and rectified within such a period. On this basis it is considered that adequate protection was given in the presence of 5 per cent. seawater in the test coolant.

Inhibitor 'B' has been used with success in engine tests at AEL, but

with strict control of its concentration. The rig tests, all of which needed early termination, did not allow for make-up of obviously depleted inhibitor. Rig testing with soluble oil concentration kept within recommended limits was not resorted to, as it was appreciated that depletion in service could on occasions be even more rapid owing to oil separation caused by either seawater ingress or exhaust gas blow-by.

Inhibitor 'C' is certainly not recommended for engines with aluminium alloy cylinder heads as gross pitting of the aluminium heater sheaths was experienced as shown in FIG. 5. This pitting was not observed on test coupons of the same alloy, thus clearly demonstrating the need for a laboratory test to include realistically hot metal surfaces.

Objective 4

One problem associated with the use of ethylene glycol antifreeze solutions is the possible corrosion of bearings in the event of these coolants contaminating engine lubricating oil. It is therefore an advantage to be able to detect such a leak at an early stage so that remedial action can be taken before serious damage occurs. To facilitate early detection a variety of additives to ethylene glycol were considered.

Rig testing showed that three potential additives rapidly lost sensitivity and this was due either to thermal instability or combination with metal surfaces. Titan yellow, another detecting agent considered, apparently increased the corrosion of cast iron and solder. The availability of the rigs thus gave a comparatively rapid and cheap means of eliminating four candidate materials which had passed simple laboratory glassware heating tests.

A method has been developed which is limited to glycol formulations containing phosphate. It is considered that, should wider interest be shown, the best approach would be to detect borate, as it is included in several formulations and could be added without detriment to most of the others.

Objective 5

One engine manufacturer has successfully overcome a flame plate corrosion problem by Kanigen (a high phosphorous nickel alloy) plating. The interiors of these cast iron cylinder heads are similarly plated and it has been reported that corrosion inhibitors incorporating phosphates are incompatible with the Kanigen. Interaction between nickel and phosphate is believed to result in a scale formation on the hottest parts of the cylinder head surface which are in contact with coolant. The thermal insulating effect of this scale results in overheating and subsequent thermal failure.

BS 3150, the antifreeze normally used when required by the Royal Navy, includes triethanolamine phosphate among its inhibitors. Squires (10) in his comprehensive study of this formulation also reports corrosion of nickel in the presence of NaMBT, the other inhibitor present. It was therefore decided to use the coolant test rigs to investigate this reported problem by having heater sheaths prepared from the same grade of cast iron as the cylinder heads and Kanigen plating their outer surfaces to the engine manufacturer's specification.

Centre wall temperature changes of these heater sheaths were then measured during normal test runs with BS 3150 and other formulations. The results obtained are summarized in TABLE IV.

BS 3150 and formulation 'X' both contain phosphate inhibitors, and the thermally insulating deposits that they formed on the Kanigen plated surfaces proved to be most tenacious. When testing these same formulations with aluminium heater sheaths the maximum temperature rise observed after 6 weeks testing was 4°C. Similar results were obtained when using higher rated heaters

TABLE IV—*Kanigen-plated heater sheath temperature increase*

Formulation	Temperature Change	Duration
BS 3150	+17°C	4 weeks
BS 3151	+ 0°C	4 weeks
'X'	+13°C	4 weeks
Inhib. 'A'	+ 5°C	4 weeks

thus confirming the reports that phosphate inhibited coolants should not be used in engines with Kanigen plated cylinder heads.

Although a small temperature rise was observed during the test with Inhibitor 'A', the removed sheaths were apparently unblemished and temperature measurements were far more consistent due to the excellent protection given to all components of the test rigs. During all of the other tests temperature fluctuations were caused by temporary deposition of corrosion products from other rig components.

One interesting observation was that the system's pressure had a marked effect on heater sheath temperature. Reducing the pressure from 700 mb to a minimum by fully opening the relief valve caused a drop in sheath temperature of approximately 8°C when the recirculating test solution was at 95°C. It is considered that this was due to pressurization raising the test solution's boiling point. This in turn reduced the amount of nucleate boiling at the heater sheath's surface and increased the proportion of cooling by forced convection which is less efficient.

Preliminary experiments with aluminium LM6 alloy heater sheaths have consistently given temperatures of 123°C ± 1°C at the beginning of a number of tests. Runs on BS 3150 have been characterized by a general increase in temperature of 4 to 5°C, whereas those on BS 3151 have not shown any significant temperature change. It is intended to repeat these tests using higher rated heaters, since by increasing the flow of cold water through the rigs' 'cold finger', the mean bulk temperature of the test solution can be maintained with a higher heat input.
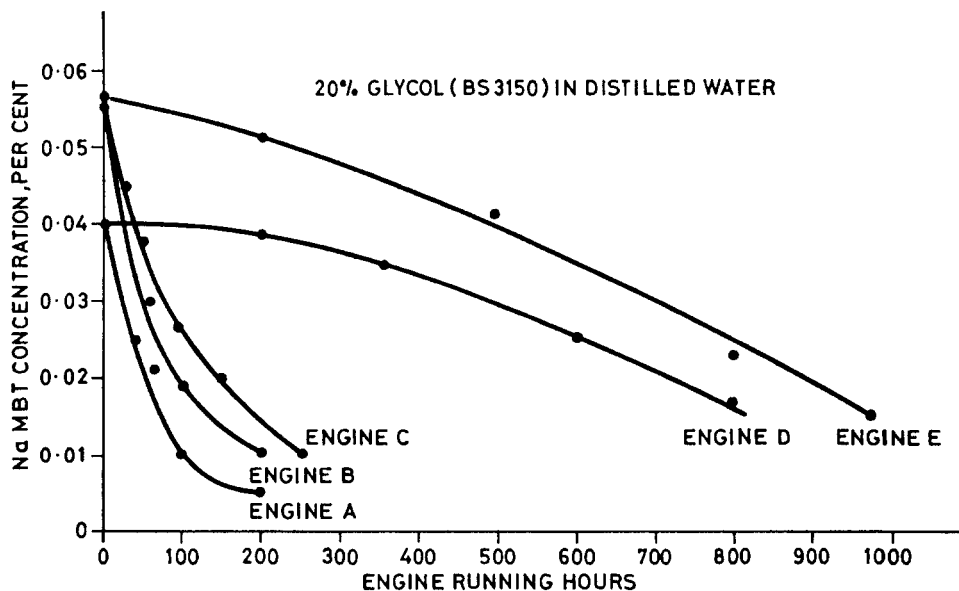

FIG. 6—TYPICAL NaMBT DEPLETION RATES FOR VARIOUS ENGINES

Engine Operating Experience

Changing priorities and their effect on staff availability have made it impossible to conduct a systematic evaluation of test-bed engine coolant inhibitors. Nevertheless, the value of inhibitor concentration control has been usefully demonstrated by a relative freedom from coolant problems on a variety of engines for several years at AEL. Therefore it is only possible to mention those aspects that can be related to the previously described laboratory tests.

Early work showed that inhibitor depletion rates were mainly dependent on engine running time, but that the rate itself could vary according to the type of engine. Particular attention was paid to the depletion rate of NaMBT in BS 3150 glycol solutions. Maintenance of its concentration above a minimum level was considered necessary to protect copper alloys; particularly as copper corrosion products were reputed to catalyze the breakdown of ethylene glycol to corrosive organic acids.

FIG. 6 records typical NaMBT depletion rates experienced with five different diesel engines:

Engine A—2 stroke, 6 cylinder, 85 mm bore, cast iron cylinder head, cast iron liners, approximate coolant volume 5 gallons.

Engine B—4 stroke, 16 cylinder, 247 mm bore, cast iron cylinder head, steel liners, approximate coolant volume 130 gallons.

Engine C—4 stroke, 6 cylinder, 247 mm bore, cast iron cylinder head, steel liners, approximate coolant volume 90 gallons.

Engine D—4 stroke, 12 cylinder, 197 mm bore, aluminium cylinder head, chromium-plated liners, approximate coolant volume 100 gallons.

Engine E—2 stroke, 18 cylinder opposed piston, 130 mm bore, aluminium cylinder block, tin-plated liners, approximate coolant volume 150 gallons.

It can be seen that the rate of NaMBT depletion was principally governed by the materials present in the cooling systems; the rate for those with a high iron content being about four times greater than for the non-ferrous materials. This experience was similar to that obtained with the coolant test rigs according to the material of the reservoir used as shown in FIG. 4.

Additions of NaMBT were made to the coolant of Engine B whenever its concentration fell below 0·01 per cent. to establish whether a useful content could eventually be maintained for a longer period. FIG. 7 shows that even after three such additions the rate of depletion was substantially the same.
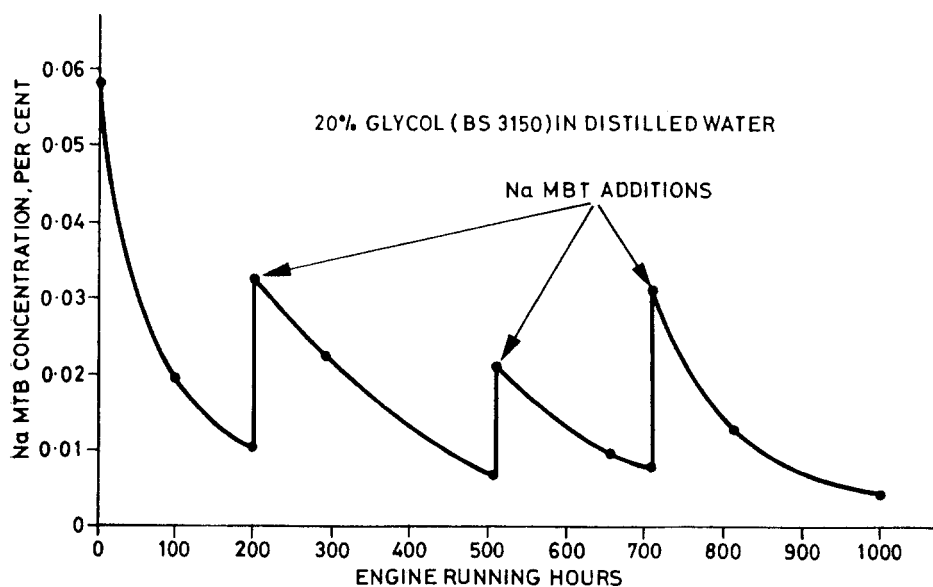

FIG. 7—NaMBT DEPLETION RATES ON ENGINE B AFTER CONTROLLED ADDITIONS

A number of tests were then conducted to investigate the importance of this rapid depletion in certain engines. Pre-weighed metal coupons were inserted near both the inlets and outlets of cylinder water jackets and reweighed at intervals. Even after prolonged running without further inhibitor additions, corrosion of copper or its alloys was negligible provided that a specific inhibitor for copper, such as NaMBT, or benzotriazole, was initially present in the coolant. In fact, a type B engine ran for over 2000 hours with 20 per cent. BS 3150 before a coolant change was necessary for reasons other than the corrosion of copper. The coolant test rigs have confirmed these results since corrosion of copper has always been very low for NaMBT-containing coolants, even when the initial concentration of 0·04–0·06 per cent. has fallen to below 0·01 per cent. early in the test period.

Although much less running has been done with benzotriazole, it has been apparent that it is just as effective an inhibitor for copper alloys as NaMBT and has a lower rate of depletion. The copper chelate film formed by benzotriazole, on which inhibition depends, is acid soluble; strict pH control is thus advisable for coolants containing benzotriazole.

Engine tests at AEL with a soluble oil inhibitor in distilled water have given good results providing that the oil concentration is maintained at levels between 0·2 and 0·5 per cent. The rate of depletion varied considerably even on similar engines, and in one case the oil concentration dropped considerably after a 10-week idle period. There is an apparent tendency for coolants thus treated to leak more readily than others. This is probably due to the considerable lowering of the coolant's surface tension by the oil addition.

Unusual Experiences

(A) Problems associated with the variety of materials that can be found in cooling systems were highlighted by an engine test on an experimental, almost colourless, inhibited antifreeze solution which had previously performed satisfactorily on the same engine.

After 140 running hours the sampling point was found to be blocked by solid contaminant and the coolant sample eventually obtained was blue in colour. Chemical analysis of the solid contaminant showed it to be about 25 per cent. silica, which was presumed to be casting sand, and salts of iron, copper and aluminium. The coolant was found to have an unusually high and most undesirable dissolved copper content and its pH had risen from 7·1 to 9·2.

Efforts to discover any difference between the two test runs revealed that the cylinder heads had been changed before the start of the last run. The new heads had been 'Tufftrided' which involved their immersion in a bath of mixed cyanide solutions. Further examination showed that the heads had not been sufficiently well water-washed before delivery. Remaining residues of alkaline cyanides trapped by unremoved casting sand had caused the coolant's pH to rise and had severely attacked the copper components. Galvanic corrosion of iron had then been accelerated by the copper-containing coolant and ferrocyanides formed had produced the blue colouration of the coolant.

(B) A dockyard report expressed concern at localized pitting observed on some cylinder liners removed from a ship's engine. On examination the pitting was found to be confined to their upper O-ring grooves and predominantly on groove faces on the water-side of the O-rings. 'Tidemarks' were also noticed on the liners, indicating that the engine had been standing idle for a long period with its coolant drained.

The geometry of the cooling system was such that after draining some residual coolant remained at the bottom of the angled liners. This then provided ideal conditions for crevice attack and differential aeration corrosion at the

liquid-air interface. Enquiries confirmed that the engine had indeed remained in a drained state during an idle period. It is therefore emphasised that it is sound practice to retain inhibited coolant in idle engines.

Inhibitor Selection

It is not the author's intention to catalogue the inhibitor formulations available or to comment on the merits and limitations of particular types. The main purpose of this paper is to emphasize the need for realistic laboratory evaluation of any formulation before its use in an engine. Brown (11) gives an excellent review of proprietary formulations and Brasher's (12) paper shows that potential new corrosion inhibitors are being examined.

Apart from corrosion protection performance and effect on heat transfer, other important aspects must be considered when selecting inhibitors:

(*i*) cost;
(*ii*) availability;
(*iii*) ease of storage, addition and concentration control;
(*iv*) ease of disposal of waste treated coolants;
(*v*) the need to obtain Department of Trade and Industry approval for any inhibitors used in cooling water used in a heat exchanger for the production of drinking water on board ship.

As a contradiction to inhibitor selection, attention is drawn to Heslop's (13) proposals which completely eliminate the use of inhibitors and depend upon the incorporation of a deionizing unit in the cooling system. The purpose of this unit is to remove water impurities and ethylene glycol breakdown products by ion exchange. Providing that distilled water is used in preparing the coolant, quite a small unit would suffice for marine diesels; though care would have to be taken not to add inhibitors to the coolant as these would rapidly saturate the unit's resins.

Comment

The concept of a standard laboratory test for inhibited coolants is a sound one, as there is a need to ensure their effectiveness in a realistic manner before introducing them into the cooling systems of expensive engines. It is, however, desirable that suppliers indicate the composition of their products. This would then reduce the prospects of an engine operator mixing two incompatible formulations that individually would pass the test.

It is considered that the proposed antifreeze test rigs are adaptable to investigate engine coolant corrosion problems in general. Rig operators are bound to be influenced by their employers' requirements in the selection of construction materials, running conditions and purity of water tested, etc. but the existence of a fully specified test will give a basis on which to judge the effect of any necessary variations.

Although the rigs were initially developed for the evaluation of inhibited antifreeze solutions, it is not surprising that the results obtained are less conclusive than those from inhibited water. Freshly prepared ethylene glycol solutions are relatively innocuous, but are gradually oxidized to form corrosive organic acids. The rate of this breakdown is largely governed by the mean coolant temperature, local hot spot temperatures, oxygen availability and copper corrosion products which can catalyze the reaction.

Therefore, in antifreeze solutions the metal corrosion rate is at first very slow, but accelerates as acid breakdown products are formed unless they are rapidly neutralized by a suitable additive. One rig operator is now investigating the value of using a linear polarization resistance method for determining corrosion rates. This takes the form of a metal probe in the top bend of the specimen hose.

In this way it is hoped to establish how the rig variables affect the oxidation of antifreeze solutions. Even with tests on inhibited water, a knowledge of corrosion rate would be valuable as metal coupon weight losses could be reasonable and similar after a stated test period for two different formulations, say 'A' and 'B'. However, if the corrosion rate of 'A' had decreased progressively, whereas that for 'B' had been negligible at first but was increasing with time, 'A' would be the preferred formulation.

Some tests have been characterized by the formation of extremely tenacious deposits on the heater sheaths, which presumably would also occur on hot surfaces in an engine's cooling system. French (14) in an investigation into the factors affecting heat transfer at a metal-to-coolant interface has shown that some inhibitors have such an adverse effect on heat transfer as to seriously increase metal operating temperatures. This is a most important aspect which the coolant test rigs can be employed to investigate. It is postulated that coolant volume-metal surface area ratios are just as important in heat transfer as in corrosion protection studies. The nature of deposits formed on heat transfer surfaces can also be influenced by other metals present in the system; so that, provided heat fluxes of the right order can be arranged, the coolant test rig should give a reliable indication of any inhibitor-induced thermal problems.

Finally, it must be stressed that corrosion inhibitors are intended to prevent rather than cure corrosion. All too often disappointing results from engine tests on laboratory recommended formulations can be traced to their introduction to a system already corroded or contaminated.

Conclusions

Numerous organizations have a variety of marine diesels under their control and many problems can arise if a different water treatment is required for each type. Therefore, there is a need for a coolant inhibitor formulation that can be used with confidence in all types of diesel engines. Engine tests can be both lengthy and expensive so that reliable laboratory tests are required.

Operational experience gained on the rigs described has shown them to be a useful laboratory tool for realistically evaluating coolant corrosion inhibitors. This is demonstrated by comparing results obtained with those from actual engine tests.

The standardization of such a test should be of considerable benefit to both suppliers and purchasers of inhibitors, but the trend to up-rate engines, coupled with the possible introduction of new alloys into cooling systems, justifies adaption of the rigs to investigate specific problems.

One of the main purposes of inhibiting engine coolants is to prevent the adverse effect of corrosion on heat transfer; so all prospective formulations should be checked to ensure that they themselves are not responsible for forming undesirable thermal barriers on heat transfer surfaces. Early results indicate that the rig described will be suitable for such checks.

Although the test can confidently be used to list inhibitors in an order of merit, much work remains to be done. There is a need to establish criteria whereby inhibitors can be rejected or recommended for use, and the effects of changing temperature, flow rate, duration, aeration and even the introduction of vibration have yet to be fully examined.

Acknowledgements

The responsibility for any statement of fact or opinions expressed in this paper rests solely with the author.

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