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Helicopter Transmission Oil Discolouration

Andrew Becker and Paul Rawson

Air Vehicles Division
Defence Science and Technology Organisation

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ABSTRACT

An increase in the incidence of abnormal discolouration of oil in ADF helicopter tail rotor transmissions has been observed and reported over the last eight years. Aircraft maintainers have initially attributed the discolouration to a range of contamination modes including incorrect fluid addition, hydraulic fluid contamination and degraded fluid. A program of work was conducted at DSTO to identify and characterise the cause of the abnormal discolouration. This report details the identification of a coloured metal quinizarate salt which forms in the aircraft transmissions under normal operating conditions and describes the mechanism of formation and some characteristics of the quinizarate salt to assist in developing maintenance programs to manage the coloured salt when observed in service conditions.

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Helicopter Transmission Oil Discolouration

Executive Summary

Effective lubrication of modern military aircraft transmissions requires the use of highly specified synthetic polyol ester lubricants. Significant effort can be expended in ensuring serviceability of these oils through a range of oil condition monitoring programs. The current oil used in many ADF helicopter transmissions meets the MIL-PRF-23699 specification and a number of specific brands of oil meeting this specification are in routine service within the ADF.

An increase in the incidence of abnormal discoloration of oil in ADF helicopter tail rotor transmissions has been observed and reported over the last eight years. The most numerous description of the discoloration was of a two phase fluid with a red-purple phase observed at the bottom of the aircraft tail rotor sight glass. Aircraft maintainers have initially attributed the discolouration to a range of contamination modes including incorrect fluid addition, hydraulic fluid contamination and degraded fluid.

A program of work was conducted at DSTO to identify and characterise the cause of the abnormal discoloration. This report details the identification of a coloured metal quinizarate salt which forms in aircraft transmissions under normal operating conditions and describes the mechanism of formation and some characteristics of the quinizarate salt.

Isolation and purification of the 'red-purple' contamination was followed by detailed chemical analysis using a wide range of chemical techniques. The red-purple material was found to be formed from quinizarin, which is a metal passivating additive found in some of the brands of oils and copper metal in solution in the oil. The copper was sourced to a bronze component in the aircraft tail rotor transmission.

DSTO has provided advice to the ADF to assist in developing maintenance programs to manage the occurrence of the coloured quinizarate salt.

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Abbreviations

DMF	N,N-Dimethylformamide
Quinizarin	1,4-Dihydroxyanthraquinone
GCMS	Gas Chromatograph - Mass Spectrometer
FTIR	Fourier Transform Infrared
GPC	Gel permeation Chromatography
m/z	Mass to charge ratio
NaOH	Sodium Hydroxide
SEM-EDS	Scanning Electron Microscopy - Energy Dispersive Spectroscopy
TRGB	Tail Rotor Gear Box

1. Introduction

Modern military aircraft place high demands on their engine and transmission lubricants. The lubricants must perform over a wide range of operational and environmental conditions and provide not only effective protection against mechanical wear but also maintain thermal, hydrolytic and oxidative stability as well as a range of performance characteristics including the ability to protect components from corrosion.

Ideally, for optimum performance, an aircraft would use different oils for its engines and transmissions, however, to reduce logistic burden, many military aircraft use a single fluid for lubrication of engines and transmissions. For the Australian Black Hawk and Seahawk aircraft the oil chosen to meet these requirements is a synthetic 5 cSt aircraft gas turbine engine lubrication oil designation OX-27; this oil is also known as NATO O-156 and US MIL-PRF-23699. The fluid also has three grades designated as standard (STD), corrosion inhibited (CI) and high thermally stable (HTS). The ADF has historically used only the 'standard' grade; however, there have been recent requirements for use of the CI and possibly the HTS grades of the oil.

The OX-27 fluid is a critically balanced fluid based on a synthetic ester base oil blended with a range of additives that provide performance enhancement for the oil. These additives include antioxidants for improved thermal and oxidative stability, boundary lubrication additives (antiwear, lubricity and extreme-pressure), anti foaming additives, anti corrosion additives and metal passivators.

Since 2003, the ADF has reported an increase in the occurrence of abnormal discolouration of oil in both Black Hawk and Seahawk tail rotor gear boxes (TRGB). The abnormal discolouration has been observed through the TRGB oil level sight glass. Instances of the purple discolouration obscuring the actual sight glass have also been reported, Appendix A and B [1]. The oil has been described as being red or purple and often two layers of oil have been noted. This observation has led to concern over contamination of the TRGB with hydraulic fluid, which on both aircraft types is a red fluid meeting either the H-515 or H-537 specification. A previous investigation into these field incidents identified one of the oil additives as potentially being the cause of the abnormal colour [1]. The additive package of the oil was examined and the metal passivator, 1,4-dihydroxyanthraquinone, commonly known as quinizarin, was found. This additive was suspected as the cause of the colour change. The quinizarin additive is also the source of the orange colour of many brands of OX-27 oil. About 50% of the MIL-PRF-23699 and DOD-L-85734 oils use quinizarin. [2]

Quinizarin is added to the oil as a metal passivator, some times also called a metal inhibitor or deactivator. Alloys that contain copper can catalyse reactions that can cause oxidative degradation of the base oil. Additives such as quinizarin and benzotriazole are common 'yellow' metal deactivators[3]. Synthetic turbine oils may contain a number of polyhydroxy anthraquinones at varying concentrations. Suitable compounds are 1,2; 1,3; 1,4; 1,5; and 1,8 - dihydroxyanthraquinone and the higher polyhydroxy substituted anthraquinones such as 1,2,4-trihydroxyanthraquinone and 1,2,5,8-tetrahydroxyanthraquinone. The 1,4-dihydroxyanthraquinone has been identified as the preferred metal passivator. The preferred concentration

of the additive is in the range 0.01 to 0.5 % w/w. [4-8]. One patent identifies the poly hydroxy-substituted anthraquinone additive to be employed in the range 0.04 to 0.5 % w/w with a minimum effective concentration of 0.035% w/w.[6]

Quinizarin belongs to the family of chelating agents that actively reduce the catalytic activity of metal ions. The mechanism of action is to react with copper and other reactive metal ions to form a stable and non reactive chelate, thus removing the catalytic potential of the metal ions. One disadvantage of chelating additives is they may accelerate the transfer of metal ions into solution [9].

Other common metal passivators are triazoles, benzotriazoles, 2- mercaptobenzothiazoles and tolutriazole derivatives[10]. These additives work via a mechanism of film forming and act to coat metals including wear metal particles surface to form a non reactive layer. If catalytically active metals, especially copper, are not 'passivated' they will catalyse oxidative degradation reactions in the oil thus reducing its service life.

To assist in ongoing maintenance actions on the aircraft a program of work was undertaken to positively identify and characterise the purple precipitates observed in the aircraft TRGB. Positive identification of the purple precipitate could then assist in identifying its source and any subsequent maintenance actions required.

2. Experimental

2.1 Helicopter Transmission Oil

The ADF may acquire a number of different brands of oil that meet the O-156 specification, a qualified products list for MIL-PRF-23699 (STD) oil lists 32 different oils that meet the specification. In ADF service only three brands of the oil are commonly used. Samples of all three oils were obtained and examined to identify the metal passivating component of the additive package.

The oil samples were extracted with 1.25 M NaOH and the resulting extract reacidified and examined using gas chromatography - mass spectroscopy (GCMS). Two of the oils were observed to change immediately from an orange to a blue-purple colour on contact with the NaOH.

Samples of discoloured oil were obtained from three Black Hawks, A25-204, A25-206 and A25-207. Photos of the oils are given in appendix A. The oils were either centrifuged or left to stand for a week with subsequent filtration through a 0.45 micron glass fibre filter to isolate the purple precipitate for further investigation. The filtered sediment was examined using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), see Appendix A.1.

The purple precipitates were washed exhaustively with hexane to remove excess oil and then methanol to remove any unreacted additives; an insoluble purple grease like residue was

observed as the end product. A portion of the purple residue was acidified with HCl and back extracted into dichloromethane. The extract was evaporated down to 100 μ L and analysed using GCMS.

2.2 Quinizarin Metal Chelate Preparation

To determine if metal salts of quinizarin were the cause of the abnormal oil colour a range of metal quinizarate salts were produced and used as standards for direct comparison against the discoloured oil. To determine the most common metals in contact with the Black Hawk and Seahawk TRGB a spectrometric oil analysis was done on a sample of discoloured TRGB oil. The results of this analysis indicated that copper, magnesium, iron and nickel were the most abundant wear metals.

All chemicals used were reagent grade. Common organic solvents, commercially available, were used without further purification. 1,4-dihydroxyanthraquinone purity $\geq 98\%$ from Sigma-Aldrich was used. The metal salts used were magnesium acetate tetrahydrate $\geq 99\%$ Sigma-Aldrich, copper (II) acetate hydrate 98% Sigma-Aldrich and nickel (II) chloride hexahydrate 97% from BDh chemicals. Two methods were used to prepare metal chelates of quinizarin [11, 12].

Chelates of each of the three metals were prepared using two methods.

For the first method, 0.004 moles of quinizarin was dissolved in 1000 mL of ethanol to which 0.004 moles of the metal salt in 500 mL of water was added with stirring. Additionally a stoichiometric amount of N-butylmethylamine was added. The solution was refluxed for 4 hours. The solution was left to stand overnight and the precipitate collected by filtration with repeated water and acetone rinsing.

For the second method, 0.02 moles of quinizarin were dissolved into 300 mL of hot dimethyl formamide to which 0.02 moles of metal salt in 300 mL hot dimethyl formamide was added with stirring. The solution was refluxed for 4 hours. All solutions were observed to darken to a red-brown colour. The solutions were left to stand for 24 hours before decanting and filtration of the precipitate. The precipitate was washed in acetone then Soxhlet extracted for at least 8 hours. The nickel and copper quinizarates were dark purple and the magnesium quinizarate was a bright red colour.

The magnesium and nickel quinizarates were soluble in methanol; however the copper quinizarate was not readily soluble in common solvents and was only partially soluble in hot DMF.

2.3 Quinizarin additive concentration

The quinizarin additive concentration in the oils was unknown and not available in the open literature. The concentration of additive in fresh oil was determined and compared to that in oils that contained the purple precipitate. To determine the amount of the quinizarin additive a chromatographic method was developed using 2-fluorobiphenyl as an internal standard and

10% solutions of the oil. A single ion monitoring technique was used quantifying the quinizarin based on response from the 240 m/z main fragment of the compound.

2.4 Instrumentation and Analytical Methods

A range of analytical techniques were used to characterise the nickel, copper and magnesium quinizarates to compare them with the helicopter oils and the precipitate obtained by filtration of the oils.

2.4.1 Gas Chromatography - Mass Spectroscopy (GCMS)

An Agilent 7890A GC coupled with an Agilent 5975C mass spectrometer was used fitted with an Agilent HP-5MS capillary column 30 m x 0.25 mm x 0.25 µm column. GCMS set up conditions were as follows; Temperature program 50°C hold 3 minutes then 20°C ramp to 300°C hold for 30 minutes. Helium carrier gas constant flow 1.2 ml/min.

2.4.2 Gel Permeation Chromatography (GPC)

A Perkin Elmer HPLC series LC pump 200 was used with a Waters model R401 refractive index detector. The GPC column was a 10 x 500 mm divinylbenzene Jordi GPC column with a DMF solvent flow rate at 1.5 mL/min. The molecular weight standards used were Polymer Laboratories polystyrene standards.

2.4.3 Fourier Transform Infrared (FTIR)

A Nicolet 5700 Fourier transform infrared spectrometer with a Smart Orbit diamond crystal ATR was used.

2.4.4 X-ray Fluorescence (XRF)

A PANalytical Minipal 4 XRF unit was used for oil analysis. Setup X-ray generator 30 kV and 300 µA with a silver filter and helium medium.

3. Results and Discussion

Synthetic polyol ester based turbine oils may change colour in service due to a number of reasons, the most commonly observed is due to degradation of the oil through thermal oxidation [13]. These colour changes are not normally due to contamination and are not always an indication of loss of performance. The oils initial colour is normally due to a combination of its additive package, rather than the colour of the base oil. Changes in chemistry of these additives and changes in the degree of oxidation of the oil are the primary drivers for the oil colour changes in service.

Other factors which can cause colour changes are the inclusion of wear metal debris and dirt which can cause a brown discolouration. Abnormal wear in bearings may cause localised hotspots which may tend to form soot which can blacken the bulk oil. Another cause of an apparent black discolouration of oil is elastomer degradation which can manifest as a very fine dispersion of elastomeric particles suspended in the bulk oil.

3.1 Oil Additive Investigation

The three different brands of oil examined displayed different reactions to the addition of metals solutions containing copper and magnesium. As the oil additive package was identified as the most probable cause of the colour change the metal passivator additive of each oil was examined. It was determined that both the Mobil Jet Oil II and the NYCO Turbonycoil 600 contained quinizarin. The BP turbo oil 2380 contained no quinizarin; however, it did contain benzotriazole, (Table 1). The benzotriazole does not form a coloured chelate with the metals. It is normally described as a film forming passivator rather than a chelating passivator.

GCMS analysis of the oils identified the additives and also identified the carboxylic acid component of the synthetic polyol ester base oil, (Figures 1 to 3). In all cases the acids were low molecular weight carboxylic acids in the pentanoic acid to decanoic acid weight range. This distribution of carboxylic acids is common in 5 cSt synthetic turbine oils. These acids are also involved in formation of the bulk precipitate as they will form metal carboxylates which have varying solubilities in the bulk oil. These carboxylates will tend to concentrate with the purple precipitate. The metal carboxylates are not purple and form a benign component of the TRGB precipitate. These metal carboxylates were further characterised by FTIR as described in section 3.2.3.

Table 1. Oil additive metal passivator type

Oil	Base Oil Colour	Metal Passivator
Mobil Jet Oil II	orange	quinizarin
BP turbo oil 2380	clear	benzotriazole
NYCO turbonycoil 600	orange	quinizarin, benzotriazole

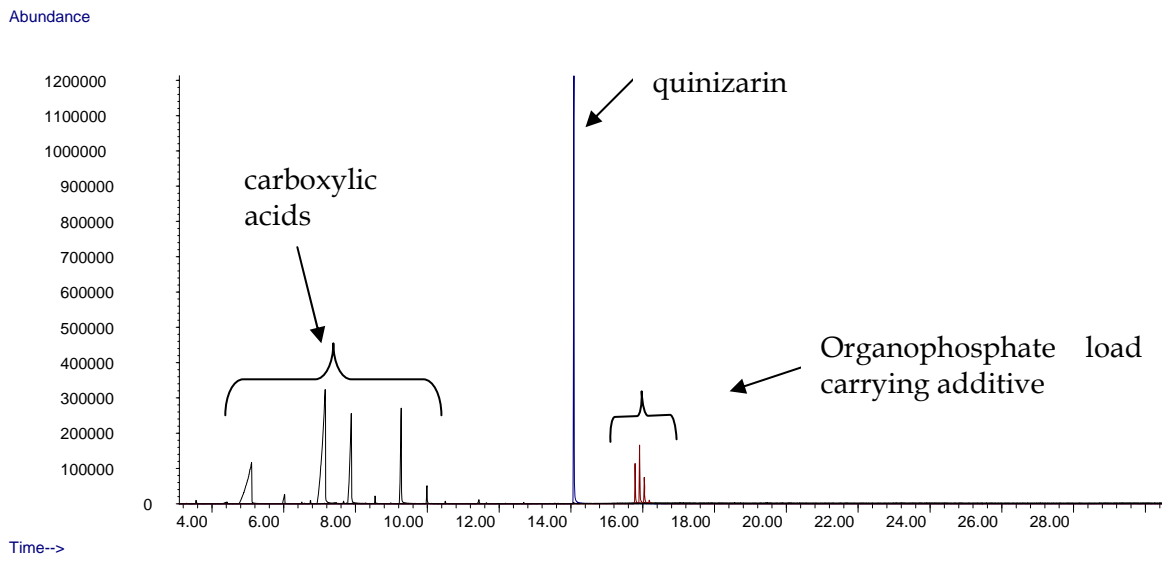


Figure 1. NaOH extract of Mobil Jet Oil II GCMS ion extracted chromatogram showing oil additives.

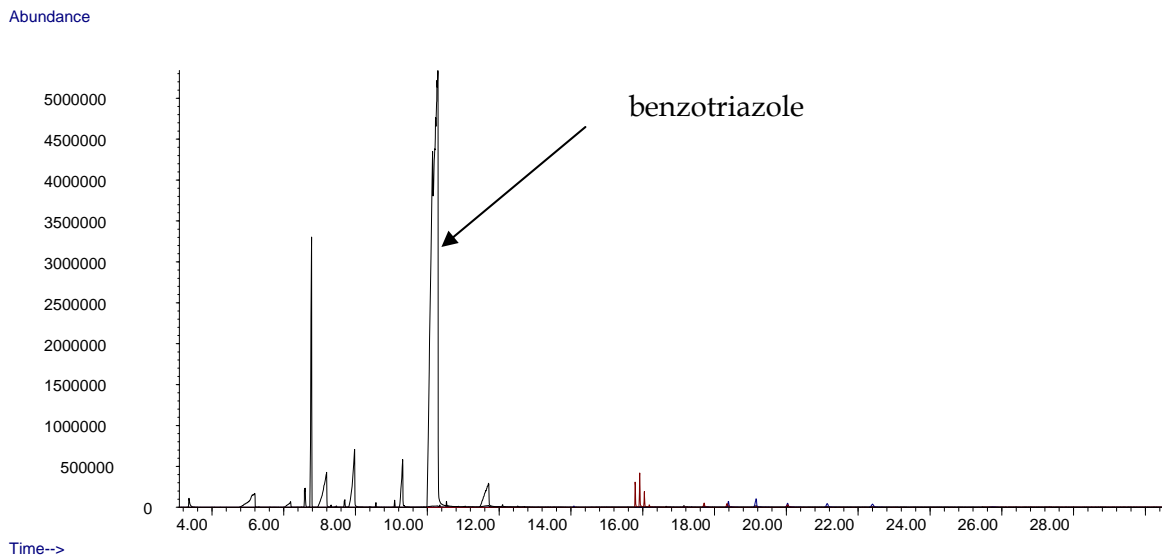


Figure 2. NaOH extract of BP turbo oil 2380 GCMS ion extracted chromatogram showing oil additives

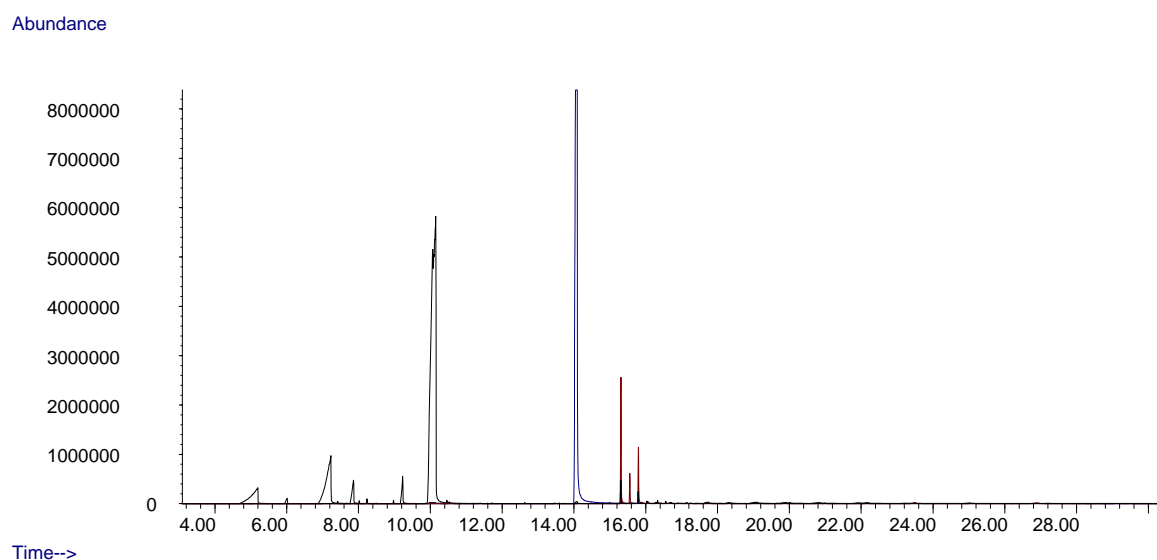


Figure 3. NaOH extract of NYCO turbonycoil 600, GCMS ion extracted chromatogram showing oil additives

To investigate the potential loss of the quinizarin from the oil in instances where the purple precipitate was observed, a range of fresh and used oils were examined and the concentration of quinizarin additive determined (Table 2). A small loss of additive was found for the two most recent TRGB precipitates obtained from aircraft A25-206 and A25-207. These oil samples were approximately 4 weeks old. The sample from A25-204 was 6 months old and was found to have lost a larger amount of the additive. It is possible that this loss was due to continued reaction of quinizarin additive with copper particles dissolving with time in the stored sample bottle and the loss additive concentration may not be a true indication of additive loss in service. The quinizarin that has reacted with the metals in solution will form a stable chelate that is not detected by this method. The quinizarin loss is consistent with the additive performing its role as a metal passivator. The losses of the additive will always occur in the presence of divalent metal ions produced due to dissolution of wear metals into the oil.

Table 2. Oil additive concentration in fresh vs. purple precipitate oils

Oil	Quinizarin, ppm
Mobil Jet Oil II	720
BP Turbo oil 2380	0
NYCO Turbonycoil 600	1160
Black Hawk engine oil (mobil jet oil II)	715
A25-207 TRGB with precipitate	550
A25-206 TRGB with precipitate	595
A25-204 TRGB with precipitate	135

3.2 Helicopter TRGB Oil Precipitate

The USN has reported a similar occurrence of what is described as a 'purple sludge' in helicopter transmissions. The 'purple sludge' is normally found as an oily film which sticks to the transmission sump walls and transmission components. This observation is consistent with the purple grease like material isolated from ADF helicopter transmissions.

The USN sludge was reported as being a formation product of acids found in hydrolysed oil and the magnesium, aluminium and copper metal components in the gearbox. This metal salt then reacts with the quinizarin to form the purple coloured sludge.

The USN 'purple sludge' was reported as "quite common in helicopter gearboxes and usually not a problem" [2]. The sludge was described as oily and smooth and no operational problems were reported as being associated with its presence in the transmissions. Instances of severe cases were reported and on subsequent investigation were found to be associated with transmissions that had large quantities of water (10% plus) and were idle for 10 to 12 months.

The Seahawk main rotor gearbox serviceability check advises 'purple discolouration of oil is not cause for replacement gear box' [14].

To examine the solubility of the copper, nickel and magnesium quinizarates once formed samples of the quinizarate standards were added to samples of fresh Mobil Jet Oil II. The samples were then sonicated for 5 minutes at 80°C to redissolve the quinizarate salt into the fresh oil. It was observed that the magnesium was readily redissolved back into the oil and the oil remained discoloured indefinitely. The nickel quinizarate was less soluble and remained discoloured for 4 days. The copper quinizarate did not redissolve back into the oil indicating that the polymerised chelate once formed would precipitate out of the oil. These observations are consistent with the molecular weight distributions of the metal salts, section 3.2.1.

3.2.1 Molecular Weight Distribution

It was suspected that wear metals in the TRGB may react with the quinizarin to form stable polymers. The length of the polymer chain being dependent on reaction conditions and metal availability. Gel permeation chromatography (GPC) of the Black Hawk precipitate and the metal quinizarate standards was undertaken to examine the formation of polymeric metal quinizarates.

Dihydroxyquinones are capable of being tetrafunctional and may form linear polymers when reacted with divalent metal ions. 1,4-dihydroxyanthraquinone will react with copper (II) ions to form a linear uncharged polymer. Difference in a variety of factors such as oil temperature, copper concentration, and oil degradation will affect the polymer chain length and a range of polymers of differing molecular weights should be expected [12]. The repeating unit for the copper polymer is given in Figure 4.

The molecular weights of the isolated purple precipitate and the metal quinizarate standards were examined to determine if the precipitate was due to the formation of insoluble polymers, (Table 3, Figure 5. It was observed that the purple precipitate did contain a range of high

molecular weight components that were similar in weight range to the three metal chelates indicating that metal quinizarate polymers had been formed.

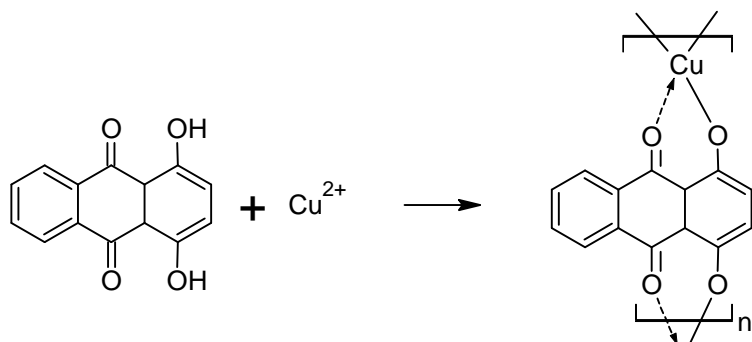


Figure 4. Reaction of quinizarin with copper to form Copper quinizarate repeating unit

Table 3. Molecular weight analysis of Black Hawk precipitate vs. metal quinizarate standards

Metal Salt	GPC analysis molecular weight	Repeating units, approx
Copper quinizarate	85240	282
	22900	75
	1930	6
	1230	4
	325	1
Magnesium quinizarate	960	4
	260	1
Nickel quinizarate	2640	9
	300	1
Black Hawk TRGB oil precipitate	59740	
	25960	
	22940	
	1250	
	1120	
	990	

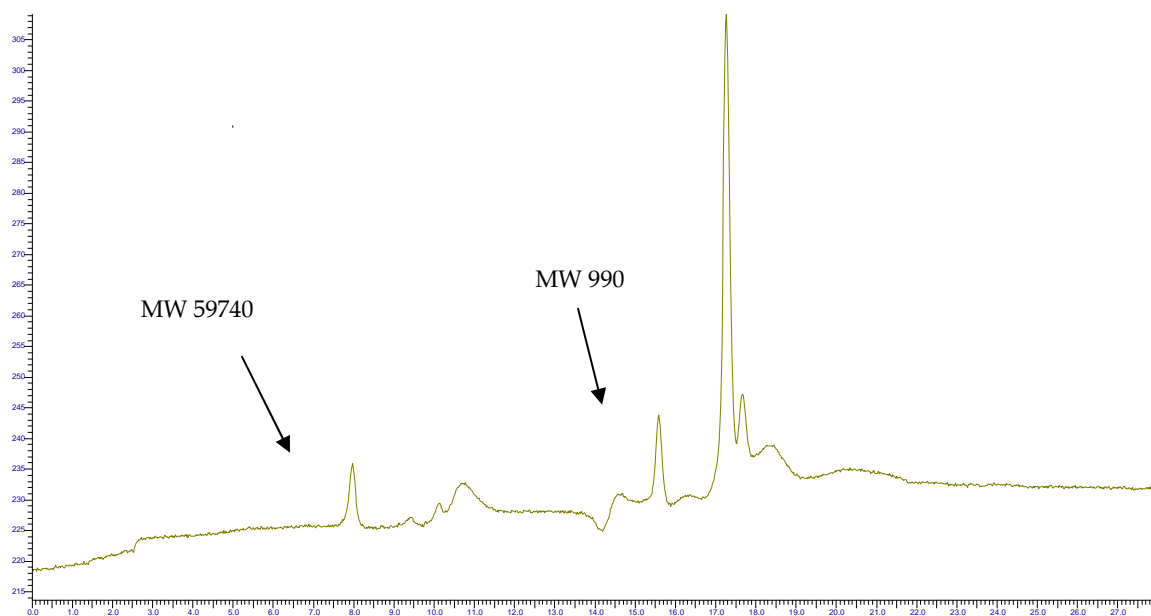


Figure 5. GPC-Refractive Index chromatogram of Black Hawk purple precipitate.

3.2.2 Addition of metal salt solutions to oil

To observe the reaction between the three brands of oil with metal salts, two solutions of copper acetate and magnesium acetate were prepared and added directly to the samples of fresh oil. The Mobil and Nycos brand oils immediately changed colour to the purple colour that matched that observed in the helicopter TRGB oils; the BP oil colour remained unchanged.

3.2.3 Precipitate analysis

Analysis of samples of the acidified precipitate obtained from Black Hawk TRGBs found it to contain quinizarin and a range of low molecular weight organic acids ranging from pentanoic to decanoic acids. The acidified purple precipitate turned orange immediately upon addition of the acid indicating that protonation of the chelate reverted the precipitate back into the quinizarin and metal.

The Black Hawk precipitate was examined by FTIR and compared against the metal quinizarate standards. Dominant peaks were observed at 1560 cm^{-1} and 1410 cm^{-1} which were attributed to asymmetric and symmetric CO_2^- stretches of a carboxylate group [15]. A shoulder peak at 1530 cm^{-1} is due to a shift in the $\text{C}=\text{O}$ carbonyl peak of the quinizarin complexing with a metal salt, Figures 6, 7 and Table 4.

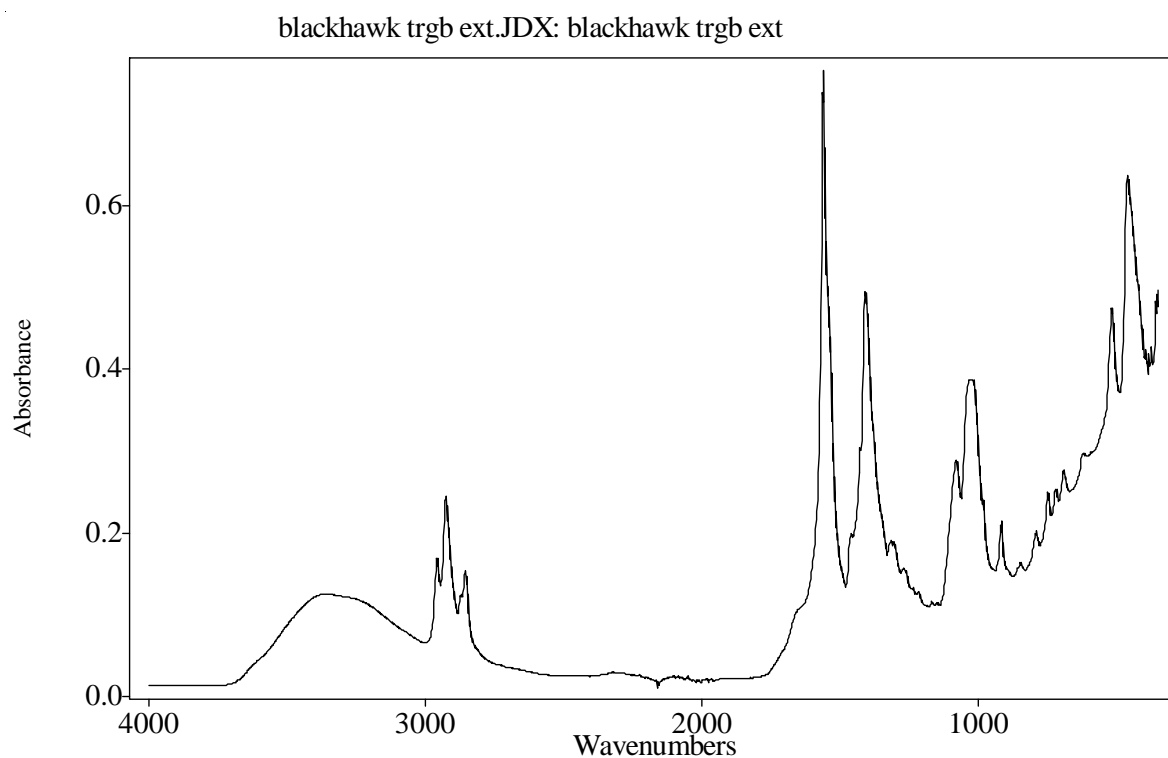


Figure 6. FTIR purple precipitate showing carboxylate group at 1560 and 1410 cm^{-1}

Table 4. FTIR shift for carbonyl region in Quinizarate chelates.

Compound	Carbonyl, wavenumbers cm^{-1}	shift
Quinizarin	1628	
Copper quinizarate	1530	98
Magnesium quinizarate	1520	108
Nickel quinizarate	1530	98

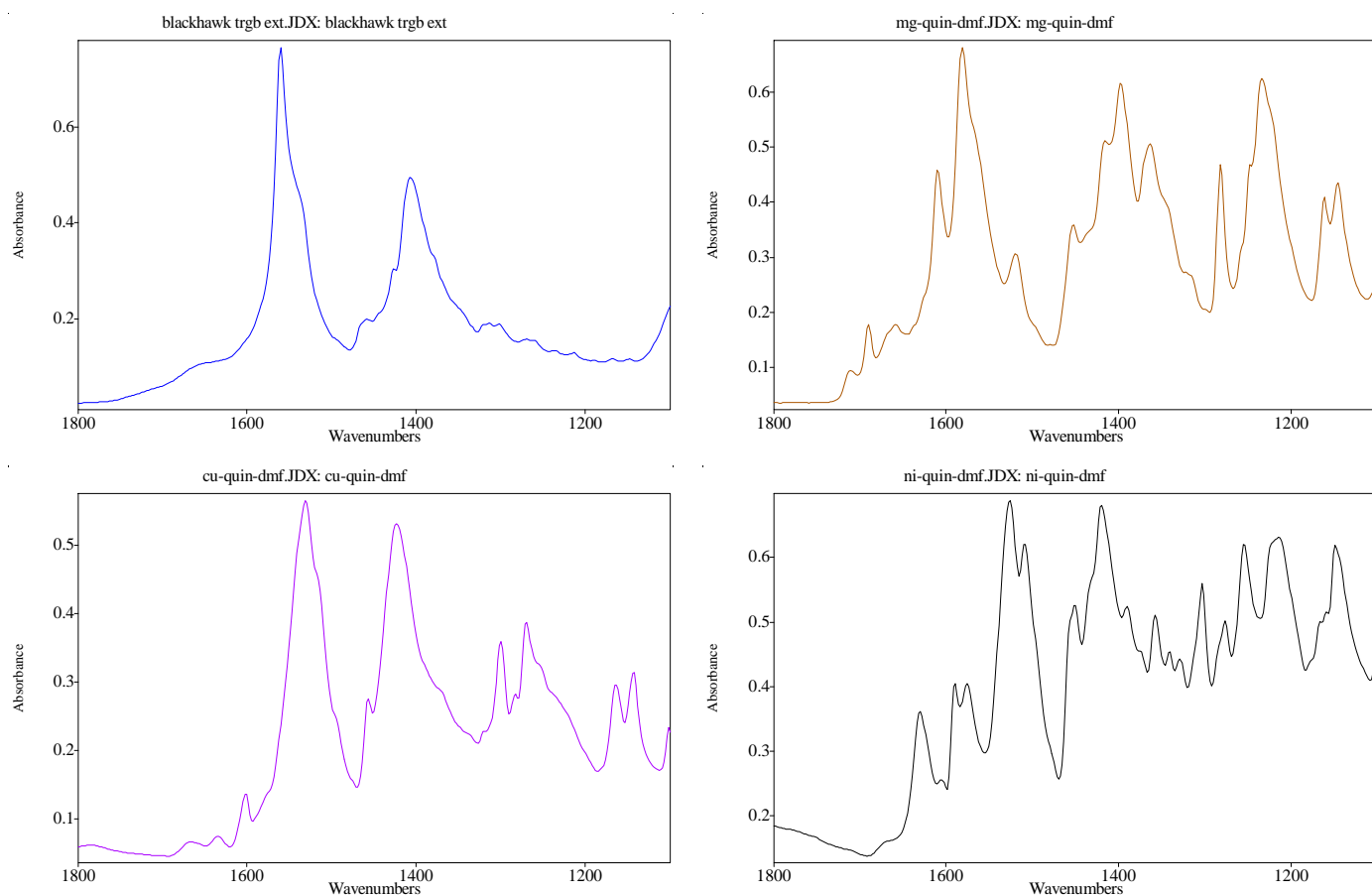


Figure 7. Showing carbonyl shift for quinizarin (top left) vs. magnesium (top right), copper (bottom left) and nickel (bottom right) salts.

The precipitate was also examined using X-Ray Florescence (XRF) to identify the metals that were present. A sample of TRGB oil from A25-206 which was purple in appearance was shaken to ensure the precipitate was evenly distributed though the sample, the sample was a uniform purple colour. Analysis by XRF identified the major metal present was copper at 0.02%. A sample of A25-207 TRGB was left to stand for four days the resultant purple precipitate concentrated down to approximately 28% by volume of the bulk oil and was examined. The concentrated precipitate was found to have a copper content of 0.110%. The only other metal observed was iron; no nickel or magnesium were found.

The rate of metal dissolution into the bulk oil is unknown and is thought to initially be controlled by the transfer of metal particulate into the oil from the metals associated with the transmission and wear debris generated from these metals in service. Rates of copper dissolution have been examined in detail by the power industry where copper causes detrimental degradation of the transformer oil. It has been reported that the rate of copper dissolution is directly influenced by the acidity of the oil, water content and the level of degradation products, including hydroperoxides in the oil [16, 17].

SEM analysis of the precipitate found a significant quantity of copper rich particles entrained in the bulk precipitate, (Appendix A). The metal particles may provide evidence for continued depletion of the quinizarin additive as they dissolve in the oil and may be the cause of the observation that once the oil has begun to show a colour change it will tend to darken with time.

3.3 TRGB Bronze bushing

The Seahawk and Black Hawk TRGB is an unfiltered gearbox and therefore is expected to accumulate both environmental ingress contamination (e.g. sand etc.) and wear debris over the oil change interval. The TRGB oil change intervals for ADF Seahawk and Black Hawk helicopters are shown in Table 5. Top up is typically required during the interval due to oil sampling and leakage.

Table 5: TRGB Oil Change Intervals

S-70B-2 Seahawk	380 flying hours or every 2 years
S-70A-9 Black Hawk	600 flying hours or every 3 years

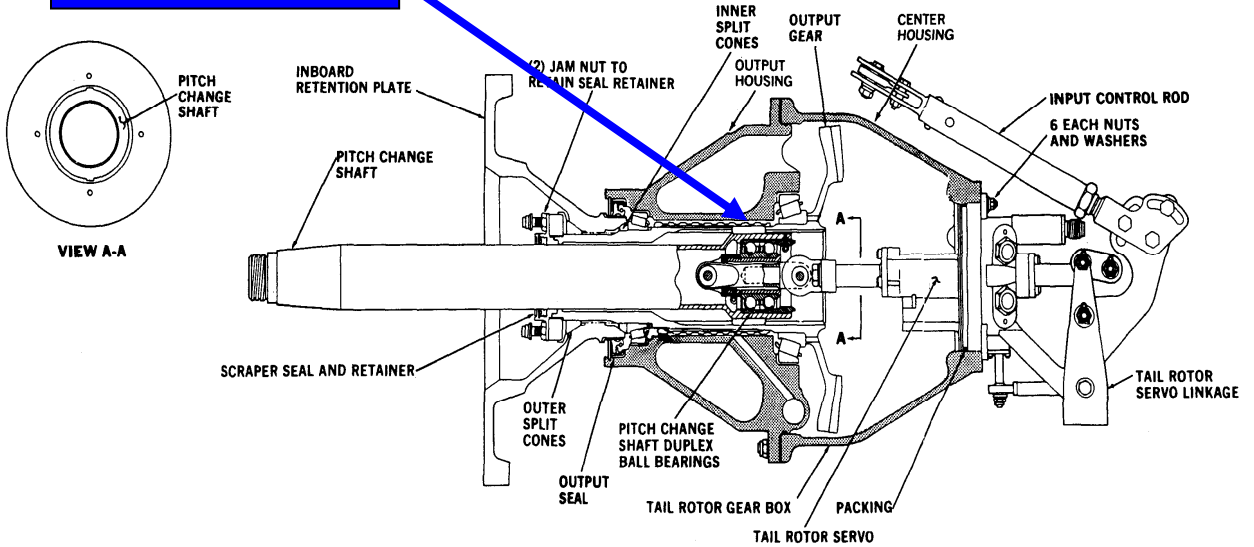
The pitch change shaft for the tail rotor blades passes through the oil-wetted section of the gearbox and is fitted with an Oilite® bronze slider bearing to accommodate sliding of the shaft (see Figure 1). It is expected that this bearing will wear in service and that the particles generated from that wear will also accumulate in the oil. At present, the degree of slider bearing wear is assessed by one of the following methods:

1. By measuring the level of copper in the Spectrometric Oil Analysis (SOA) reports. This oil analysis technique is currently only applied to ADF Seahawk aircraft. The technique is limited to detecting particles less than 8 micron (approximately), however it should detect slider bearing wear. The relative movement of the Oilite® bearing is exclusively sliding and therefore any debris generated is expected to be within the detectable range of SOA. Historical SOA results from Seahawk confirm that copper is being detected (see Figure 2).
2. By visual inspection and dimensional check as part of the routine flight controls inspection. This inspection specifically contains limits for nicks, dents, scratches and outer diameter wear [18].

There is currently no indication that the Oilite® slider bearings are experiencing any abnormal wear. Wear particles accumulating in the oil due to normal in-service wear of the slider bearing would be expected to react directly with the quinizarate and form the purple discolouration/deposit since the bronze bearing material is copper-rich. The serviceability check for the TRGB specifically states that purple discolouration is not a reason for rejecting the gearbox [14].



Oilite® Slider Bearing



TAIL ROTOR SERVO INSTALLATION

CS 1797

Figure 7: Cross-section of Seahawk/Black Hawk TRGB showing location of Oilite® slider bearing

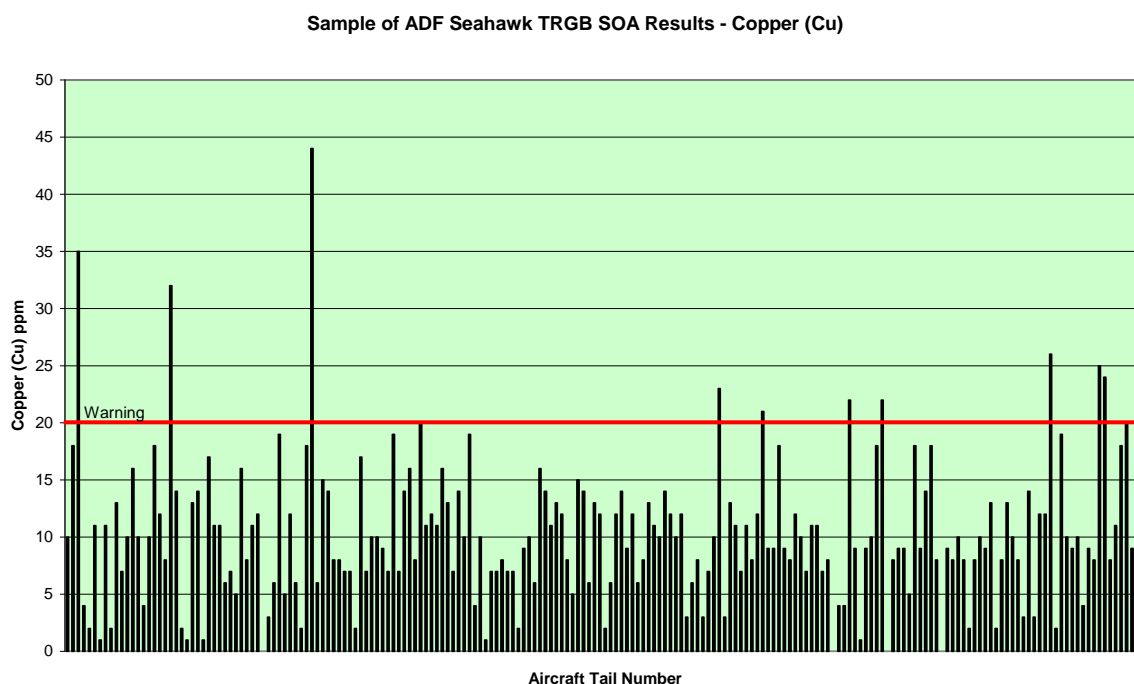


Figure 8: Sample of ADF Seahawk TRGB SOA Results for Copper (Cu)

4. Conclusions

The purple discolouration observed in Black Hawk and Seahawk TRGBs is due to the formation of coloured chelates of the metal passivating oil additive quinizarin. The 'two oil phases' described by maintainers are caused by precipitation of insoluble polymeric forms of the metal chelates, most probably copper metal, and are not due to contamination with hydraulic or other incorrect transmission fluids. Not all MIL-PRF-23699 fluids contain quinizarin and if the discolouration is considered significant a suitable non-colour forming version of the MIL-PRF-23699 oil may be sourced. The precipitate is non abrasive and will always form in normal service with oils containing this metal passivator additive.

5. Recommendations

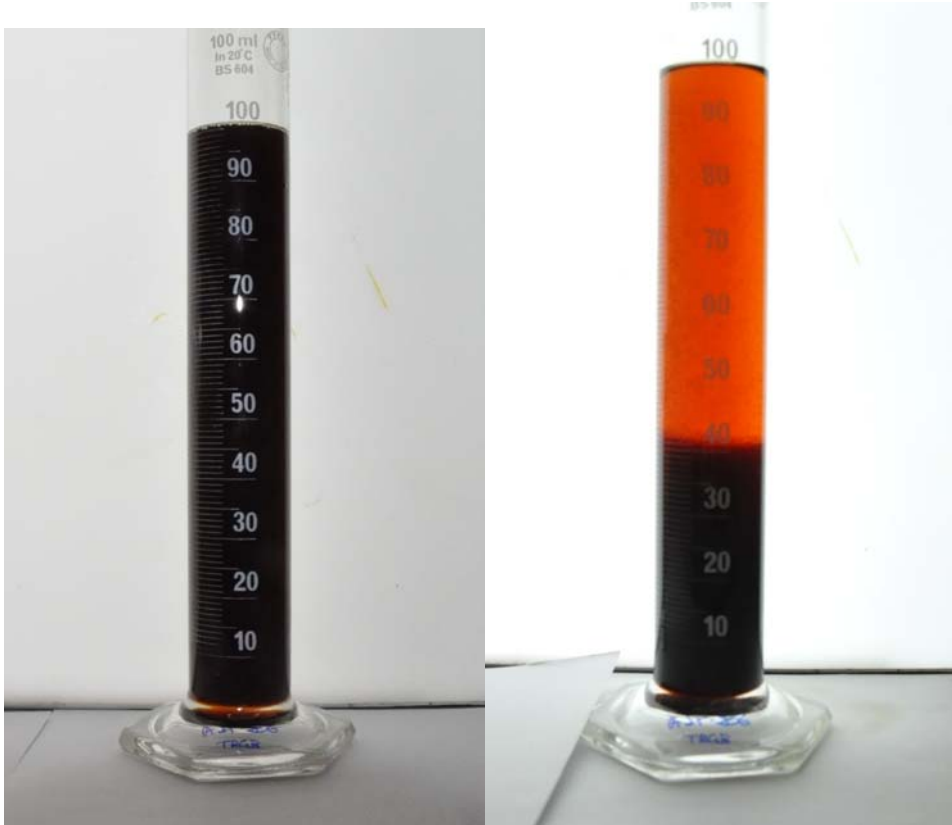
1. As transmission oil discoloration may still occur due to cross contamination with incorrect fluid, such as red coloured hydraulic fluids, and other reasons not related to quinizarate salt formation, samples should still be sent to DSTO when concern about oil discoloration exists.
2. Overhaul facilities should be requested to advise the relevant SPO where a substantial build up of the purple sludge is observed so that oil gallery integrity can be ensured.

3. The TRGB Bronze bushing should be checked for excessive wear if the TRGB oil continues to discolour significantly after an oil change out.

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Appendix A: Helicopter TRGB Oil Images



Figures A1 and A2. A25-206 TRGB oil before and after 48 hours standing



Figure A3. MIL-PRF-23699 Fluids

Left to right: Fresh BP Turbo oil 2380, fresh Mobil Jet Oil 2, Discoloured A25-207 TRGB oil. 50% A25-207 TRGB oil mixed with BP Turbo oil 2380.



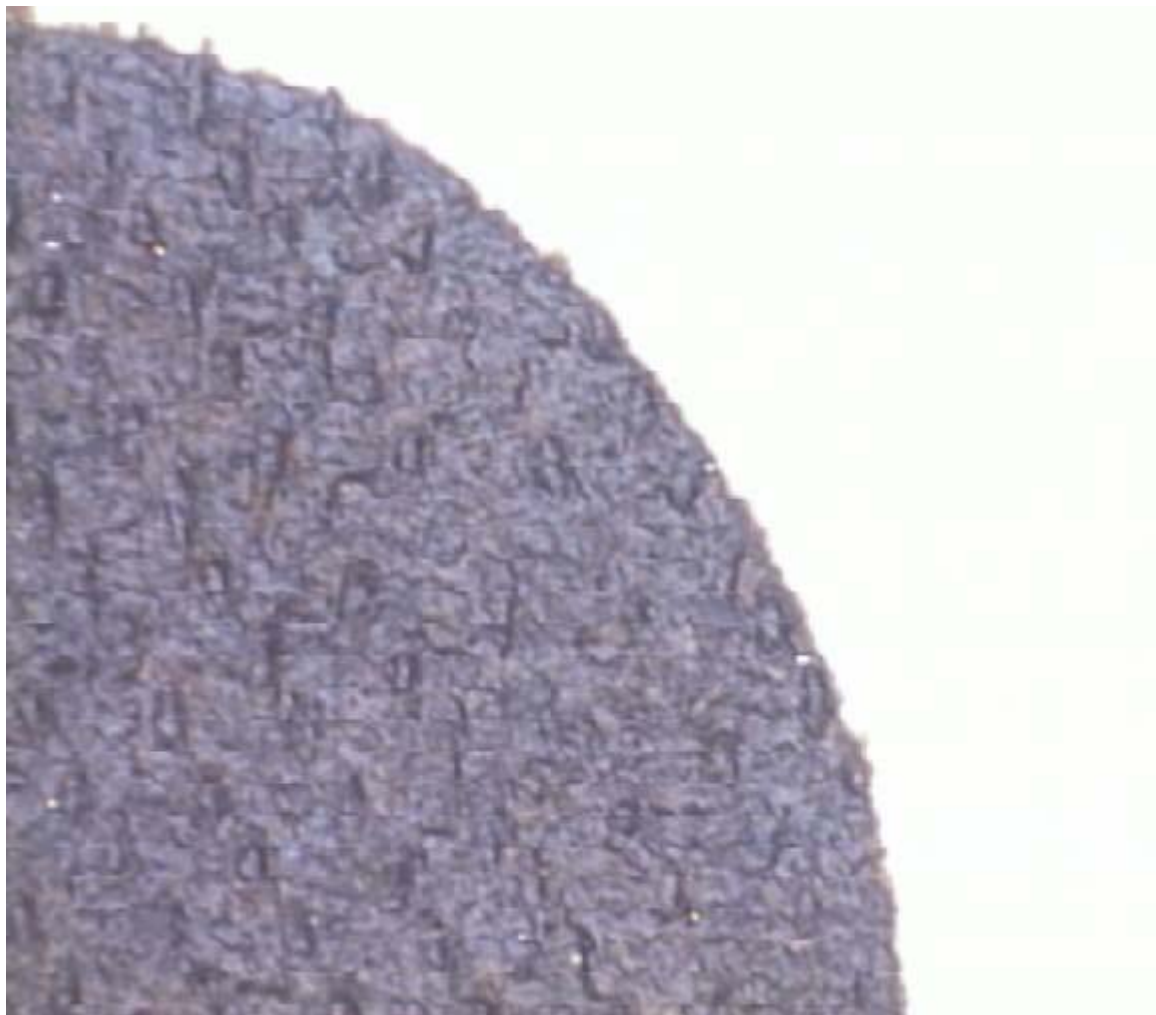
Figure A4. MIL-PRF-23699 Fluids after 48 hours standing.

Left to right: BP Turbo oil 2380, Mobil Jet Oil 2, Discoloured A25-207 TRGB oil. 50% A25-207 TRGB oil mixed with BP Turbo oil 2380. Note the BP Turbo oil 2380 was observed to darken in colour after 48 hours.



Figure A5. Oil samples from left to right: Fresh Mobil Jet Oil II; A25-107 TRGB; A25-204 TRGB; A25-107 TRGB with precipitate (samples from 2005 archive photo)

A.1. SEM Analysis of purple precipitate



FigureA 6. Filtered and methanol washed "purple" precipitate

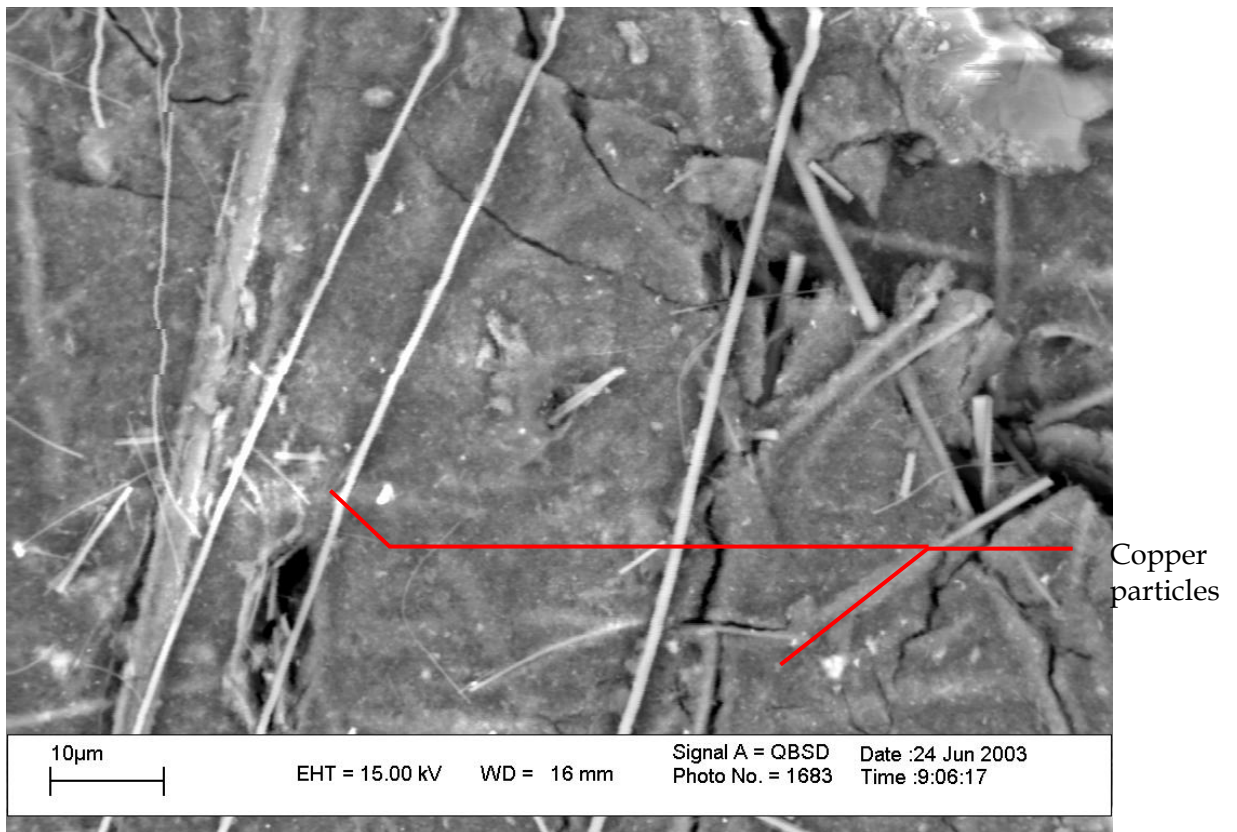
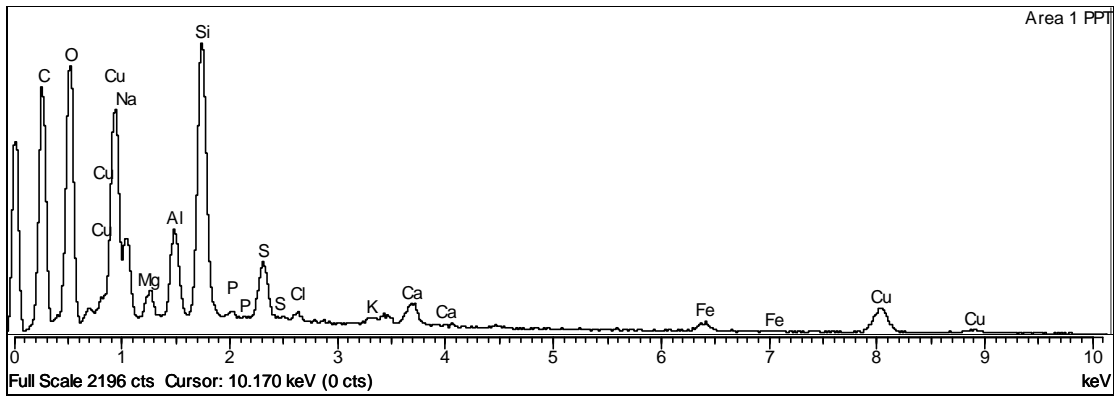


Figure A7: Backscatter Electron Image of purple precipitate



FigureA8: X-ray Scan of MTRG Oil Precipitate, from Figure A7.

(Note the peaks associated with Si, Na, Al, Ca, O and K are at least in part due to the filter media). The C, Cu, Mg, S and Fe is associated with the precipitate

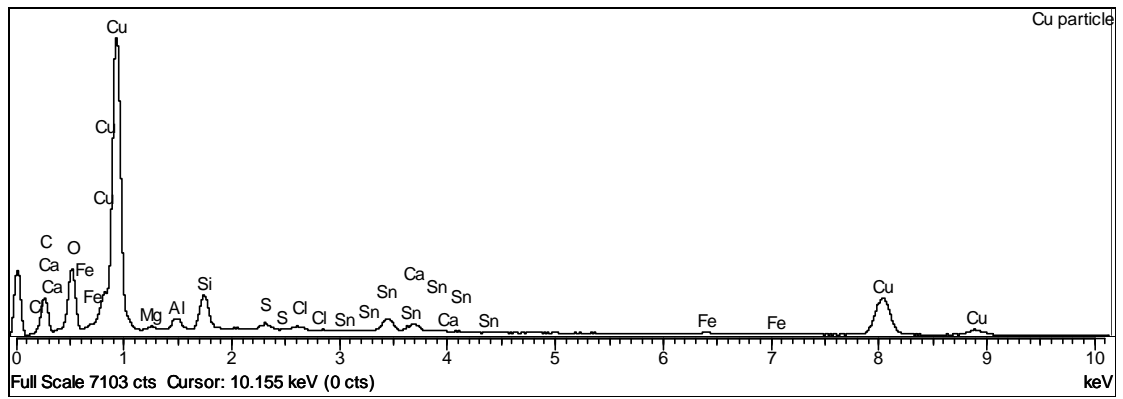


Figure A9: EDS scan of Cu/Sn Rich Particle, from Figure 7

Appendix B: Sight Glass Stain Analysis

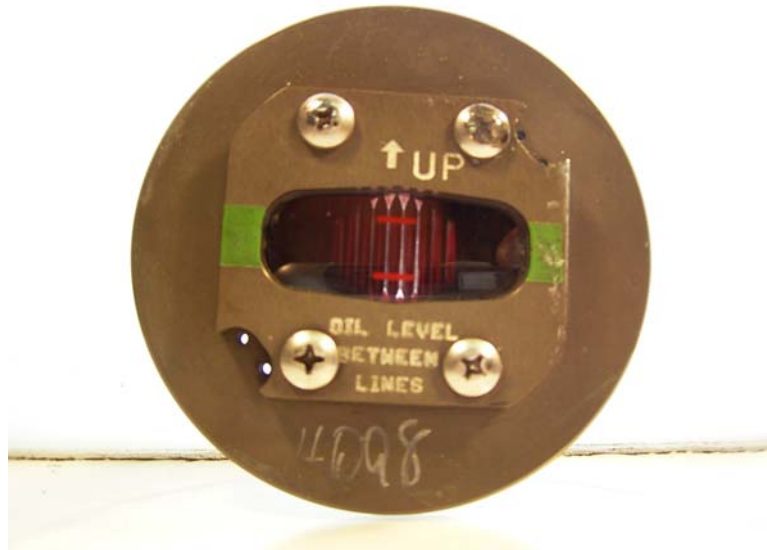


Figure B1. Sight glass from a Black Hawk, rear lit showing obscuration with red stain

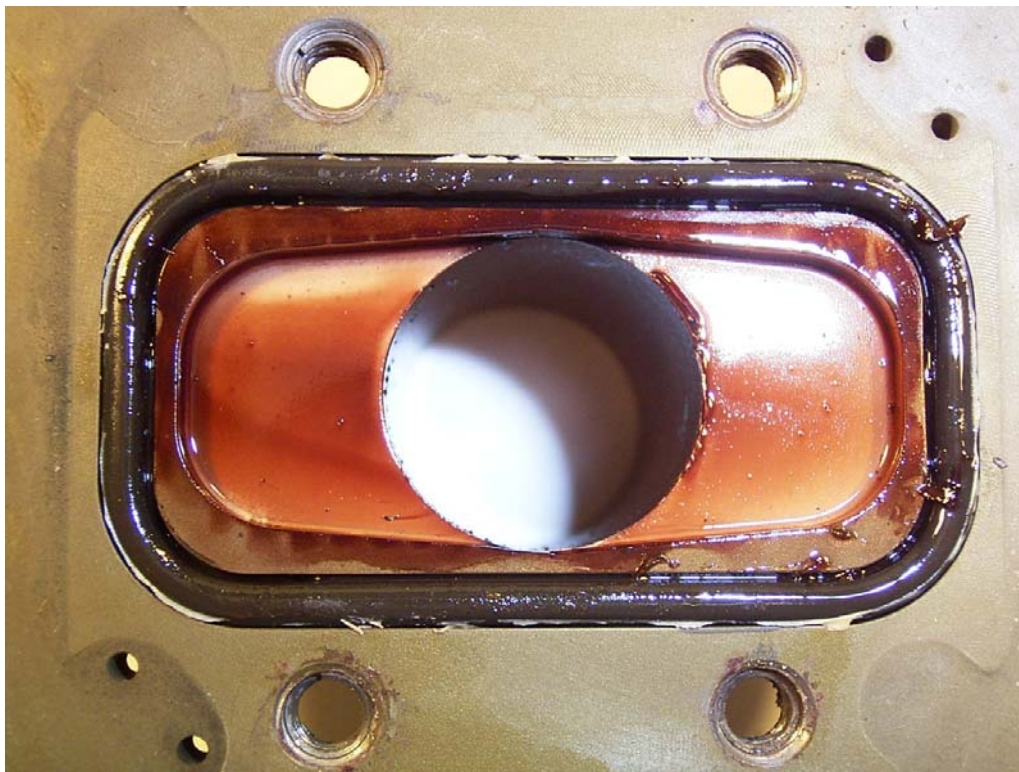


Figure B2. Sight glass, rear plate

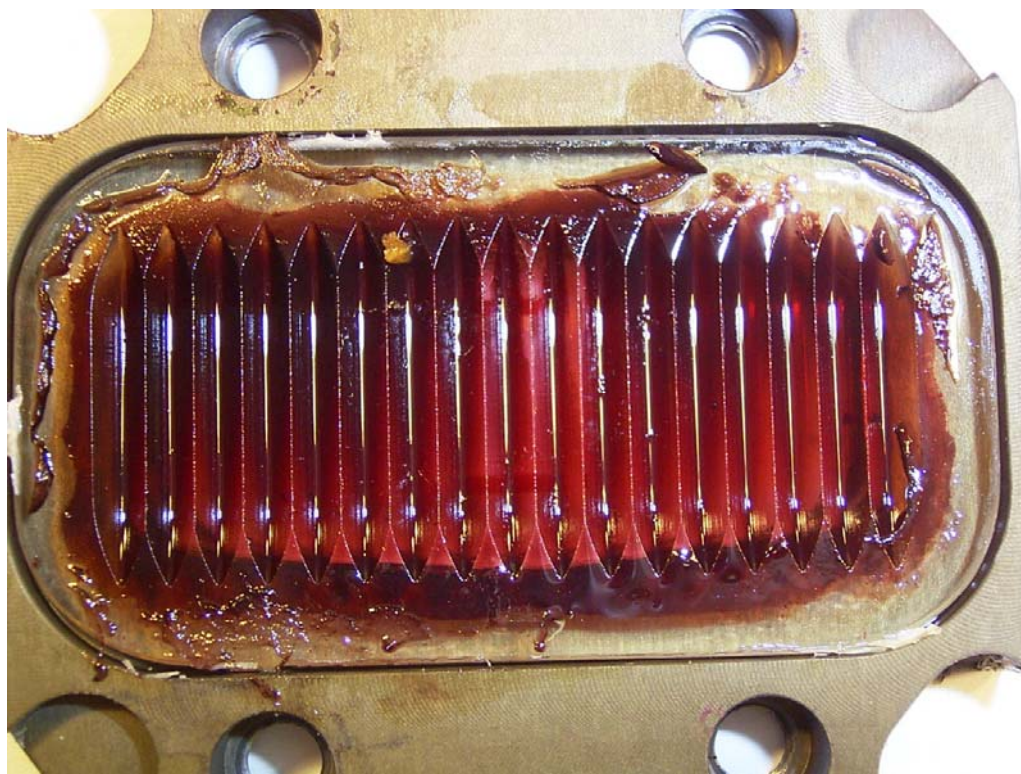


Figure B3. Sight glass inside face showing red stain and white grease like deposit

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19. ABSTRACT An increase in the incidence of abnormal discolouration of oil in ADF helicopter tail rotor transmissions has been observed and reported over the last eight years. Aircraft maintainers have initially attributed the discolouration to a range of contamination modes including incorrect fluid addition, hydraulic fluid contamination and degraded fluid. A program of work was conducted at DSTO to identify and characterise the cause of the abnormal discolouration. This report details the identification of a coloured metal quinizarate salt which forms in the aircraft transmissions under normal operating conditions and describes the mechanism of formation and some characteristics of the quinizarate salt to assist in developing maintenance programs to manage the coloured salt when observed in service conditions.					