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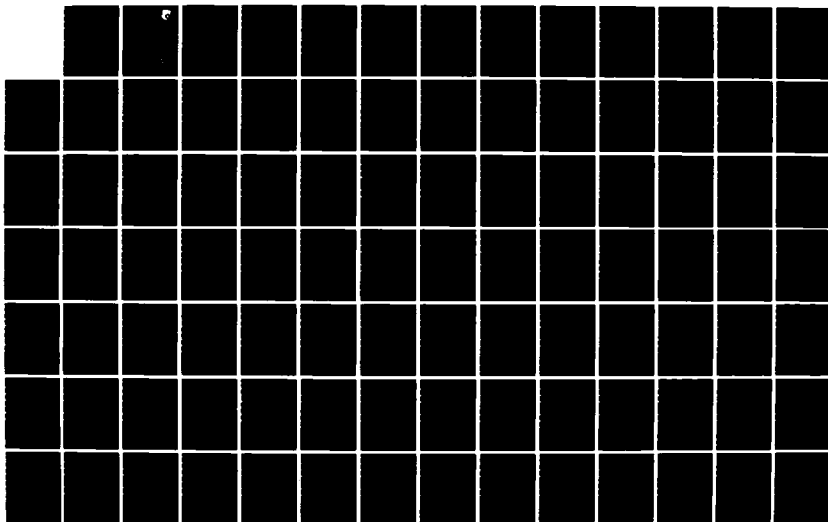
CHARACTERIZATION OF USED MIL-L-7808 LUBRICANTS(U)
DALTON AND CO (SYNTHETIC PRODUCTS) LTD BELPER (ENGLAND)
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F49620-81-C-0064

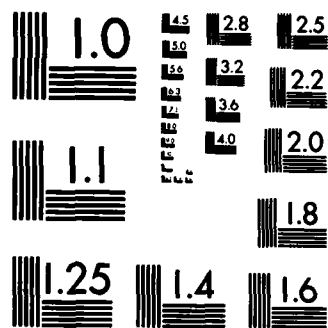
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CHARACTERIZATION OF USED MIL-L-7808 LUBRICANTS
AD-A158 624



DALTON & COMPANY
(SYNTHETIC PRODUCTS), LIMITED
SILKOLENE OIL REFINERY
BELPER, DERBYSHIRE DE5 1WF, ENGLAND

MAY 1985

FINAL REPORT FOR PERIOD MAY 1981 - DECEMBER 1984

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This technical report has been reviewed and is approved for publication.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The objectives of this effort were: (1) development of a minimum quality specification for acceptance of used MIL-L-7808 lubricants for reprocessing by the Dalton process and (2) assessing the proportion of reclaimable lubricant from samples collected from a wide distribution of USAF bases where no special precautions were taken to exclude contamination outside the engine environment. Based upon Dalton experience, a minimum quality specification was established and inspection techniques were defined. Seventy-one (71) five-gallon samples of used lubricant were provided Dalton for the assessment of reclaimability. Of the samples received, 19.7 percent were reported as being unsuitable for reprocessing during the laboratory screening process. Details of the screening process along with a proposed used oil specification are presented. It was concluded that the foaming requirements in specification MIL-L-7808 would be the most likely factor which will influence the proportion of used lubricant which can be reclaimed by the Dalton technology. Yield for this batch of material was 80 percent						
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of feedstock which is significantly lower than the 95 percent achieved during the previous program. This lower yield is probably due to the method of sampling and points out the need for special segregation and handling procedures if reprocessing is to be economically practical.

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PPFFACE

This report describes the work performed by Dalton and Company (Synthetic Products), Ltd., Belper, Derby, England, under U. S. Air Force Contract F49620-81-C-0064. The report covers work during the period from 1 May 1981-31 December 1984.

The effort defined "A Minimum Quality Specification for Acceptance of Used MIL-L-7808 Lubricants for Reclamation by the Dalton Technology" was sponsored jointly by the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories (AFWAL/POSL), Air Force Systems Command, Wright-Patterson AFB, Ohio, and the European Office of Aerospace Research and Development, Air Force Office of Scientific Research (EOARD/LNT), Air Force Systems Command, London, England. The work was carried out under Project 3048, Task 304806, Work Unit 30480628. Project managers for this effort were Lt Col O. W. Mancarella, EOARD/LNT, and Mr H. F. Jones, AFWAL/POSL. Dalton and Company, Ltd., project managers were Mr R. A. Micallef and Mr A.T.B.P. Squires.

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LIST OF ABBREVIATIONS

Dalton	Dalton & Company (Synthetic Products) Limited
STM	Supplement Test Method
VCC	Volatile Contaminant Content
GLC	Gas Liquid Chromatography
VHC	Volatile Hydrocarbon Content
EH	2-Ethylhexanol
bp	Boiling Point
MOC	Mineral Oil Content
TMP	Trimethylol Propane
DOS	Diethylsebacate
TLC	Thin Layer Chromatography
RR	Rolls-Royce
MQPI	Minimum Quality Preliminary Inspection
MQFI	Minimum Quality Final Inspection
SAP	Saponification Value
KV	Kinematic Viscosity in Centistokes
Sp. Gr.	Specific Gravity
HPLC	High Performance Liquid Chromatography
cSt.	Centistoke
LAB	Laboratory
ppm	Parts Per Million
DODP	4,4'-Diocetyldiphenylamine
PAN	Phenyl-1-Naphthylamine
MOPAN	N-4-Octylphenyl-1-Naphthylamine
DOPT	3,7-Diethylphenothiazine

LIST OF ABBREVIATIONS (continued)

NADOPT	N-Allyl-3,7-Dioctylphenothiazine
NBDOPT	N-Benzyl-3,7-Dioctylphenothiazine
PTZ	Phenothiazine
BTZ	Benzotriazole
ABA	Anthranilamide (2-Aminobenzamide)
QZ	Quinizarin (1,4-Dihydroxyanthraquinone)
TTP	Tritolyl Phosphate
DRG	Drawing

SUMMARY

Promising results have been obtained in a research programme conducted under USAF contract during 1 May 79 - 31 May 81 by Dalton & Company (Synthetic Products) Limited into the feasibility of reclaiming used MIL-L-7808 turbine engine lubricant to the quality of virgin lubricant as defined by MIL-L-7808. The yield of reclaimed lubricant was 95% of used lubricant feedstock which was collected under close supervision from USAF aircraft at Lakenheath and Upper Heyford in the UK.

The present report covers the results of a second research programme carried out under USAF contract by Dalton, with the objectives of (a) developing a minimum quality specification for acceptance of used MIL-L-7808 lubricants for reclamation and (b) assessing the proportion of reclaimable lubricant from samples collected from a wide distribution of USAF bases where no special precautions are taken to exclude contamination outside the engine environment.

Based upon Dalton experience, a scheme was devised for the minimum quality specification, details of which are presented. This comprises a preliminary and final inspection scheme designated MQPI and MQFI respectively.

The MQPI firstly places a sample into one of three groups viz., Group I (Abnormal Appearance), Group II (Normal Appearance/Abnormal Odour) and Group III (Normal Appearance and Odour). The grouped sample is then examined in accordance with the MQPI by a procedure which differs for each group, but which, for any group, determines whether the sample is to be rejected as unreclaimable, or examined further in accordance with the MQFI which is more critical.

The MQFI directs the sample into one of five Categories defined ultimately in terms of foaming propensity and chlorine content, and numbered from 1 to 5 in ascending order of confidence in the reclaimabilities of these categories of used lubricant.

Orthodox test procedures were employed wherever possible for examining the samples of lubricant supplied but, for the purpose of the minimum quality specification, it was necessary to develop three additional procedures, the development and significance of which are described and discussed in the report, and the finalised details for which are presented as Supplement Test Methods (STM) in the Appendices.

These procedures comprise:-

STM No. 1 for the determination and elimination of Volatile Contaminant Content (VCC) defined as those materials in used turbine engine lubricant which are completely or partially removed by Process 1 of the Dalton reclamation technology. It is shown that components of contaminants boiling below 235°C @ 760 Torr are completely removed.

STM No. 2 for the determination of Volatile Hydrocarbon Content (VHC) defined as those hydrocarbon contaminants in used turbine engine lubricant which are more volatile than n-hexadecane boiling @ 287°C. This procedure is employed for rapidly screening out from MQPI Group III samples those containing insignificant concentrations of volatile contaminants where there is no need to eliminate the latter by means of STM No. 1 which is applied to all other samples.

STM No. 3 for the determination of Mineral Oil Content (MOC). Samples of used turbine engine lubricants containing more than 5% w/w mineral oil in excess of hydrocarbons boiling below 235°C @ 760 Torr are rejected by the MQFI as unreclaimable.

Seventy-one samples of used lubricants received at the Dalton Refinery over the period 81 May 30 - 82 October 31 were supplied by the USAF for the assessment of reclaimability. Four of these were rejected by the MQPI, one containing over 80% water, one containing 36% VCC and one consisting of mineral oil which, upon closer examination, was concluded to be mainly hydraulic fluid MIL-H-5606B. Closer examination of the fourth rejected sample indicated that this had been taken from arisings of MIL-L-23699 lubricant excessively contaminated by mineral oil.

The volatile contaminant contents of the unrejected samples ranged from less than 1 to 20%. Isolation of these by means of STM No. 1 yielded clear mobile fluids smelling of kerosene hydrocarbons, and ranging in colour from water-white to strong yellow.

Application of the MQFI, after removal of VCC from the sixty-seven samples which had not been rejected by the MQPI, directed ten to Category 1 (Reject), thirty to Category 3 (High Foam, Low Chlorine) and twenty-seven to Category 5 (Low Foam, Low Chlorine).

Closer examination of Category 1 samples indicated that six had been taken from MIL-L-23699 samples, three of which were excessively contaminated by mineral oil, and that the remaining four samples had been taken from MIL-L-7808 arisings excessively contaminated by mineral oil.

The foaming propensities of Category 3 samples ranged from 80 to over 500 ml. foam, only three of which produced foam volumes less than 100 ml. None of these samples exhibited a foam-collapse time greater than 60 secs.

The foaming propensities of Category 5 samples ranged from 10 to 70 ml. foam, and none of the samples exhibited a foam-collapse time greater than 35 secs.

The chlorine contents of both Categories 3 and 5 samples were less than 0.01% except for one of the samples in Category 3 which contained 0.10% chlorine.

Results obtained upon determination of saponification values indicate, as a first approximation, that the base-stock components of 33% of the samples in Category 3 were predominantly polyol esters, and those of the remaining 67% were mixtures of diesters and polyol esters. Similarly, the results indicate that the base-stock components of 37% of the samples in Category 5 were predominantly polyol esters, those of 59% were mixtures of diesters and polyol esters, and those of the remaining 4% were predominantly diesters.

Quinizarin in significant concentration was found in only four of the samples in Category 3, and in only two of the samples in Category 5. HPLC analysis for other inhibitors revealed significant concentrations of 4,4-dioctyl diphenylamine and phenyl-1-naphthylamine (PAN) in all of the samples of both these categories. The only other inhibitor found was N-4-octylphenyl-1-naphthylamine, the concentrations of which, however, in all the samples were too small to be effective.

Category 3 and Category 5 feedstocks were prepared by blending together the samples in each of these respective categories. The two feedstocks were then processed separately in the Dalton reclamation plant, the yield of processed material amounting in each case to 80% of feedstock.

The foaming propensities of the processed feedstocks were 40 ml./9 secs. and 25 ml./5 secs. foam vol./collapse time for Categories 3 and 5 respectively, i.e., well within the foam requirements of MIL-L-7808. HPLC analysis showed that no losses in inhibitor contents had occurred during the processing.

The final step of the reclamation technology viz., additive treatment, was carried out for the purpose of compensating depletion of inhibitors and other additives which may have occurred during usage of the lubricants. This comprised incorporating into each of the two processed feedstocks benzotriazole, tritolyl phosphate and PAN in concentrations derived from experience, but which, in the case of the last two additives, were limited by the foaming propensities of the feedstocks and the tight restriction on foaming imposed by MIL-L-7808. The influence of these additives on foaming propensity is illustrated. The reclaimed products amounted to 294 and 239 kg for Categories 3 and 5 respectively, and were submitted to AFWAL for evaluation. Satisfactory results were obtained from a partial evaluation by Dalton.

1. Introduction

Promising results have been obtained in a research programme (1)* conducted under USAF research contract No. F.49620-79C-0073 during the period 1 May 1979 to 31 May 1981 by Dalton & Company (Synthetic Products) Limited, hereafter abbreviated "Dalton", into the feasibility of reclaiming used MIL-L-7808 turbine engine lubricant to reproduce the quality of virgin lubricant as defined by MIL-L-7808.

Both diester and polyol-ester base lubricants featured in the collections of used lubricant which were taken from USAF aircraft based at Lakenheath and Upper Heyford in the UK.

Application of the Dalton technology produced a reclaimed product amounting to 95% of the used lubricant feedstock, but intentionally, the latter had been collected in clean vessels under close supervision to reduce the hazard of contamination by other materials employed at the two bases. The programme, therefore, demonstrated the efficacy of the technology in reducing to insignificant levels trace elements and lubricant degradation products, but it did not, of course, provide information about the proportion of reclaimable lubricant which would be available on average from arisings of used lubricant collected under conditions where no special precautions are taken to exclude contamination by materials outside the engine environment.

The present report covers a research programme carried out by Dalton with the objectives of:-

- (a) Developing a minimum quality specification for acceptance of used MIL-L-7808 lubricants for reclamation.
- (b) Assessing the proportion of reclaimable lubricant from used samples collected from a wide distribution of USAF bases where no special precautions are taken to exclude contamination by materials outside the engine environment.

2. Test Methods

References to the test methods employed in carrying out the research are given in the text. Every attempt was made to employ ASTM standard procedures where possible, and a number of Rolls-Royce evaluation techniques were also employed where appropriate. Summaries of the latter and their significance have been given in (1).

It was necessary, however, in formulating a minimum quality specification relevant to the Dalton reclamation technology, to develop methods for determination of volatile contaminant content, volatile hydrocarbon content and mineral oil content. These are

* Numbers in parentheses denote references at end of report.

referred to in the text as supplement test methods (STM), and are explained and discussed below.

2.1 STM No. 1 - Determination and Elimination of Volatile Contaminant Content (VCC)

Used turbine engine lubricant may contain contaminants which are more volatile than the components of the original lubricant composition, and which are removed by vacuum-steam stripping in carrying out Process 1 of the reclamation technology (1). Examples are moisture and kerosene-type hydrocarbons which are of most frequent occurrence, but occasionally chlorinated hydrocarbons and other industrial solvents may be present.

It is necessary to eliminate significant concentrations of volatile contaminants before carrying out quantitative inspection of used lubricant samples since otherwise the dilution effect of the contaminants will complicate interpretation of the results, which will differ from those obtained after Process 1 of the reclamation technology.

Elimination of volatile contaminants from lubricant samples is normally carried out at Dalton in a steel fabricated pilot plant stripper designed to correlate approximately with the Process 1 plant, and to provide an approximate measure of VCC on a volumetric basis. This pilot plant was not intended as a laboratory test method, but was adequate for feedstocks of known composition and history when collected under special conditions devised by Dalton. It was, therefore, not considered to be suitable as a test method for inclusion in the minimum quality specification, especially since it does not lend itself readily to the determination of VCC on a weight basis, and employs superheated steam which may not be available in some laboratories.

Exploratory work was, therefore, carried out with laboratory glassware equipment to establish conditions for distilling off volatile contaminants while at the same time satisfying the following requirements:-

- (a) No degradation of the lubricant shall occur at the heat-transfer site.
- (b) No refluxing of volatile contaminants or condensation of any of the vapour thereof shall occur before the vapour at the maximum temperature of the test has passed over the stillhead into the condenser.
- (c) Lower boiling fractions of the lubricant base-stock shall not pass over the stillhead.
- (d) The proportion removed of the volatile contaminants content of the lubricant shall be not less than the proportion removed by the Dalton pilot plant stripper, and not more than the proportion removed by the Dalton reclamation plant.

With regard to (d), the investigation was conducted with samples of a polyol-ester/diester lubricant base-stock blend coded ATL.9102* to which were added known amounts of Avtur kerosene type turbine fuel complying with DERD.2494 (Issue 8). The latter was chosen as the experimental contaminant because Process 1 of the Dalton technology removes all but the last 2% comprising the high boiling components of this material whereas the pilot plant stripper, which is a little less effective, removes about 96% of Avtur contamination. Diesters in general are more volatile than the polyol-ester lubricant base stocks, and the choice of ATL.9102 ensured that this was taken into account in satisfying requirement (c).

The work carried out established the basis for design of a definable test method, the apparatus and procedure for which was then optimised and detailed as STM No. 1, which is given in Appendix A. Briefly, the method involves heating, in prescribed glass apparatus, approximately 450 mls of the test sample to 195°C in a current of nitrogen under an absolute pressure of 8 to 12 Torr, the VCC being determined from the loss in weight of the test sample.

The method was assessed by determining, strictly in accordance with Appendix A, the VCC of each of three standards prepared as below. Tests were carried out on the standards before, and after application of the method, to determine the effect of the latter upon the lubricant employed in the standards.

Samples of the standards were run also in the pilot plant stripper so that the results furnished by each technique could be compared.

Standards

- A. 1862.2 g standard B were blended with 446.2 g Avtur kerosene type turbine fuel to produce an Avtur Content of 19.3% w/w.
- B. This standard comprised a polyol/diester base lubricant coded ATL.9102* to which no other material was added.
Avtur Content = nil.
- C. 1863.0 g standard B were blended with 47.1 g Avtur fuel to produce an Avtur Content of 2.47% w/w.

The Avtur fuel employed in standards A and C conformed to DERD.2492 (Issue 8), and the results of a distillation which was carried out in accordance with ASTM/IP 086/123 are plotted in Fig. 1.

Results and Discussion

The results furnished by the two techniques for the volatile

* Supplied by AFWAL under Contract No. F.49620-79C-0073.

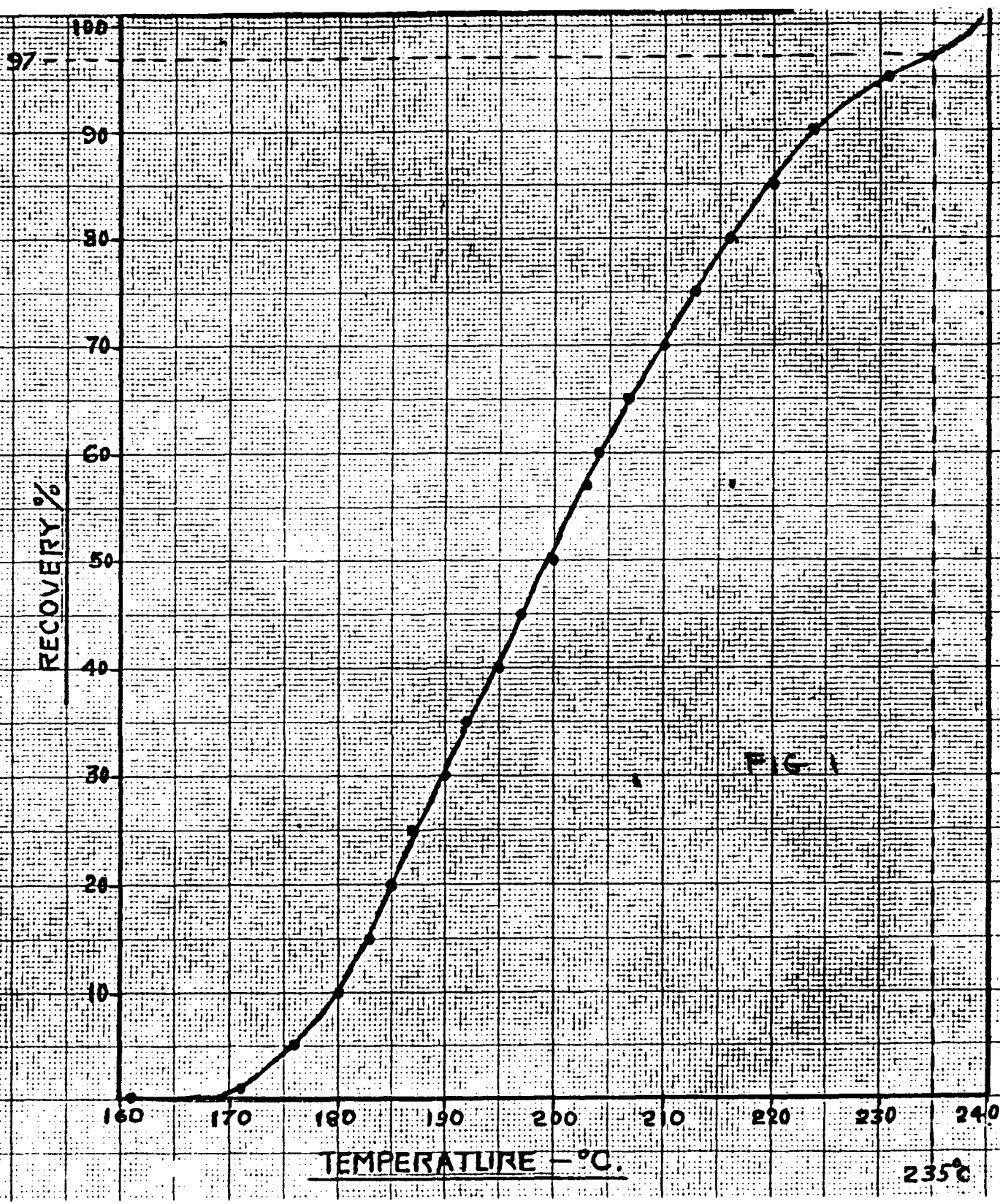


Fig. 1 - Distillation (Joint ASTM/IPD86/123) of Avtur Kerosene Type Turbine Fuel (DERD 2494)

contaminant contents of the three standards are presented in Table I in which are also presented the viscosities and total acid numbers of the standards before, and after application of each technique.

Considering firstly the volatile contaminant contents obtained by STM No. 1, it is seen that these represent 98 and 96% w/w of the Avtur contents of A and C respectively, while the result for B may be regarded as insignificant since, in accordance with STM No. 1, it would be reported as less than 0.1% w/w. The figures for A and C fall only marginally short of the results experienced with Avtur contaminated feedstocks in Process 1 of the Dalton reclamation technology and are, therefore, concluded to be satisfactory.

Taking the average, viz., 97% as the proportion by weight removed of Avtur originally present, volatile contaminants may be defined for practical purposes as contaminants boiling below 235°C at 760 Torr as represented by the abscissa of the 97% ordinate in Fig. 1. Thus, according to this definition, the least volatile contaminant approximates closely in boiling point to n-tridecane boiling at 235.5°C.

Considering the volatile contaminant contents furnished by the pilot plant stripper, these are less satisfactory in that they represent only 79 and 85% w/w of the Avtur contents of A and C respectively, and the result for B is too high to be ignored. These poor results are thought to be due to substantial weighing inaccuracies in view of considerable difficulties which were encountered in attempting to obtain reliable weight measurements with the metal pilot plant stripper.

It is seen from similar comparisons in the case of total acid number that whereas no significant change occurred upon application of STM No. 1, the pilot plant stripper produced substantial increases. These increases are thought to be due to partial hydrolysis of the lubricant, for the dryness of the steam supplied to the pilot plant is somewhat questionable in contrast with the superheated steam supplied to the production plant in which no increase in TAN takes place; some early work conducted by Rolls-Royce and Dalton on 3 cSt. diester and 5 cSt. polyol ester lubricants showed that these were not hydrolysed by water at temperatures exceeding 100°C provided the water existed entirely in the vapour phase, whereas the converse took place in the presence of liquid phase water.

Presented in Table II are the results of additional tests carried out on the three standards before, and after the application of STM No. 1. It is seen, after taking into account the initial and residual Avtur contents of the appropriate standards, that the application of STM No. 1 was successful in not producing significant alterations in the specific gravity, saponification value, DODP and PAN contents of the lubricant in the standards.

TABLE I

Standard	Avtur Content % w/w	VCC % w/w by:-		KV in cSt @ 210°F			TAN - mgKOH/g (Titrated with Aqueous Standard Alkali)		
		STM No. 1	Laboratory Pilot Plant Stripper	Before Stripping	After Stripping by:-		Before Stripping	After Stripping by:-	
					STM No.1	Lab Pilot Plant Stripper		STM No.1	Lab Pilot Plant Stripper
A	19.3	19.0	15.2	2.26	3.39	3.38	0.08	0.09	0.39
B	Nil	0.07	0.51	3.44	3.44	3.41	0.10	0.10	0.25
C	2.47	2.38	2.03	3.23	3.43	3.43	0.10	0.11	0.17

TABLE II

Standard	Specific Gravity 60°F/60°F		Saponification Value mgKOH/g		DODP %		PAN %		
	Avtur Content % w/w	Before Application of STM No. 1	After Application of STM No. 1	Before Application of STM No. 1	After Application of STM No. 1	Before Application of STM No. 1	After Application of STM No. 1		
A	19.3	0.911	0.941	229	283	0.91	1.14	0.45	0.54
B	Nil	0.941	0.941	286	287	1.12	1.13	0.55	0.54
C	2.47	0.938	0.941	279	286	1.10	1.12	0.54	0.55

2.2 STM No. 2 - Determination of Volatile Hydrocarbon Content (VHC)

STM No. 1 fulfills the purpose of removing volatile contaminants sufficiently from used lubricant test samples so that results obtained upon inspection of the latter are not greatly influenced by the dilution effect of such contaminants. The method furnishes reliable and consistent results for VCC, and by isolating the latter from a large test sample, facilitates identification of the volatile contaminants if need be. The method is not, however, as rapid as might be wished for routine inspection in that only two determinations at most can be accomplished by one operator in a working day, the time involved being largely taken up in cooling the flask assembly and contents, and cleaning out the equipment for the next determination.

The dilution effect of one percent volatile contaminants upon inspection results is not great enough to justify the time expended in stripping off concentrations not exceeding this level, and it was decided that sufficient accuracy in the inspection results at these low concentrations of VCC would be obtained so that it was then necessary to apply STM No. 1 only to samples containing more than one percent VCC. This could not be implemented, however, without some means of rapidly screening out such samples from those containing lower concentrations of VCC, and the feasibility of a GLC screening procedure was investigated.

Differences in the response factors of contaminants of different chemical type were found, as was expected, to be too great to permit routine determination of the total of their concentrations by integration of the peaks obtained on one chromatogram. This difficulty does not arise with contaminants having the same response factor, and since kerosene-type hydrocarbons are the contaminants most frequently encountered in used arisings of turbine engine lubricant, a GLC method for determination of volatile hydrocarbon content (VHC) was developed as below. This led to a definition of VHC differing somewhat from what would be expected from the definition of VCC in the case of lubricant in which the volatile contaminants comprise hydrocarbons only but, while not in every case providing a true estimate of VCC, the method was concluded, after having taken into account certain other considerations, to be adequate for screening purposes as explained later.

2.2.1 Background to Development of GLC Screening Procedure

The initial objective was a GLC procedure for differentiating used lubricant samples containing more than one percent VCC from those containing less than this concentration of volatile contaminants.

A Perkin-Elmer Sigma 115 gas chromatograph with basic facility was employed, and the chromatograms illustrated in Figs. 2, 3 and 4 were firstly obtained for Avtur, Avcat and Avtaq turbine fuels respectively, in gaining familiarity

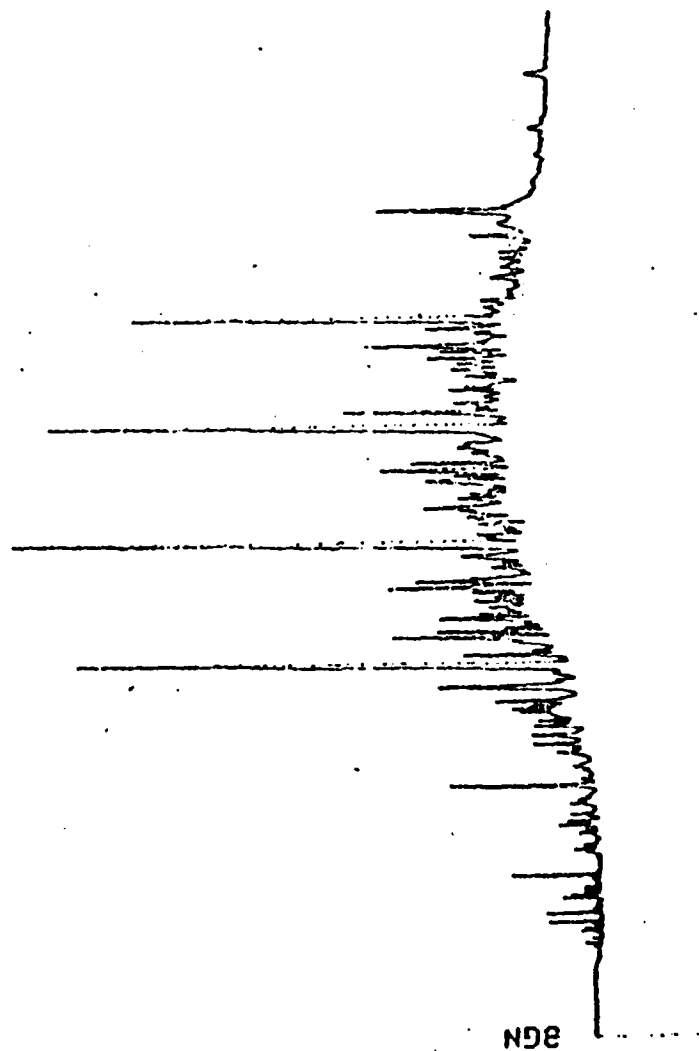


Fig. 2 - Avtur Gas Chromatogram

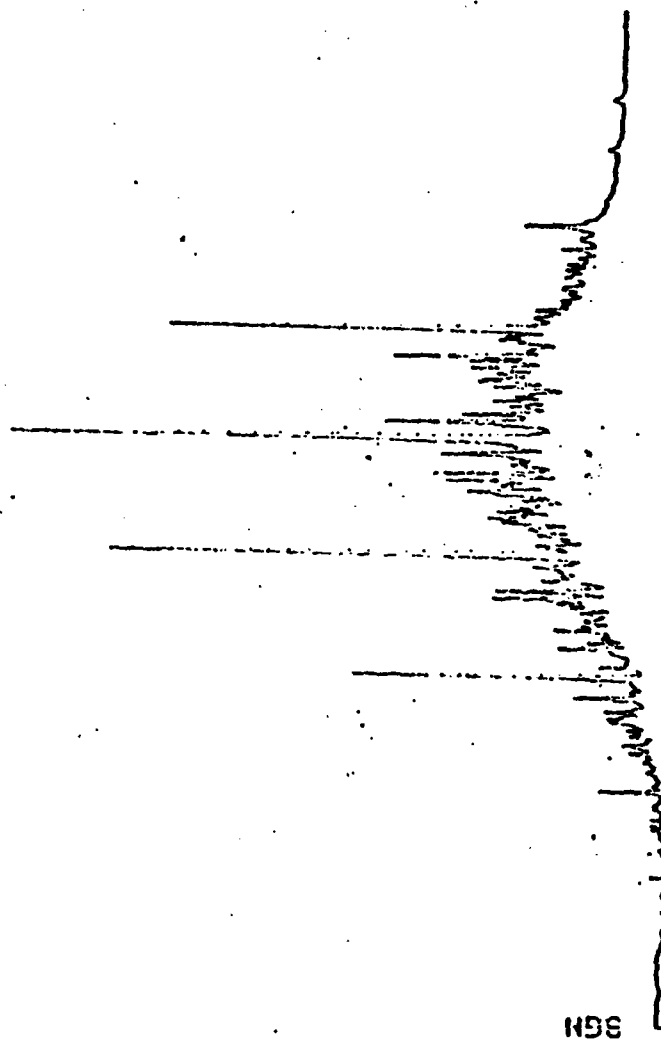


Fig. 3 - Avcat Gas Chromatogram

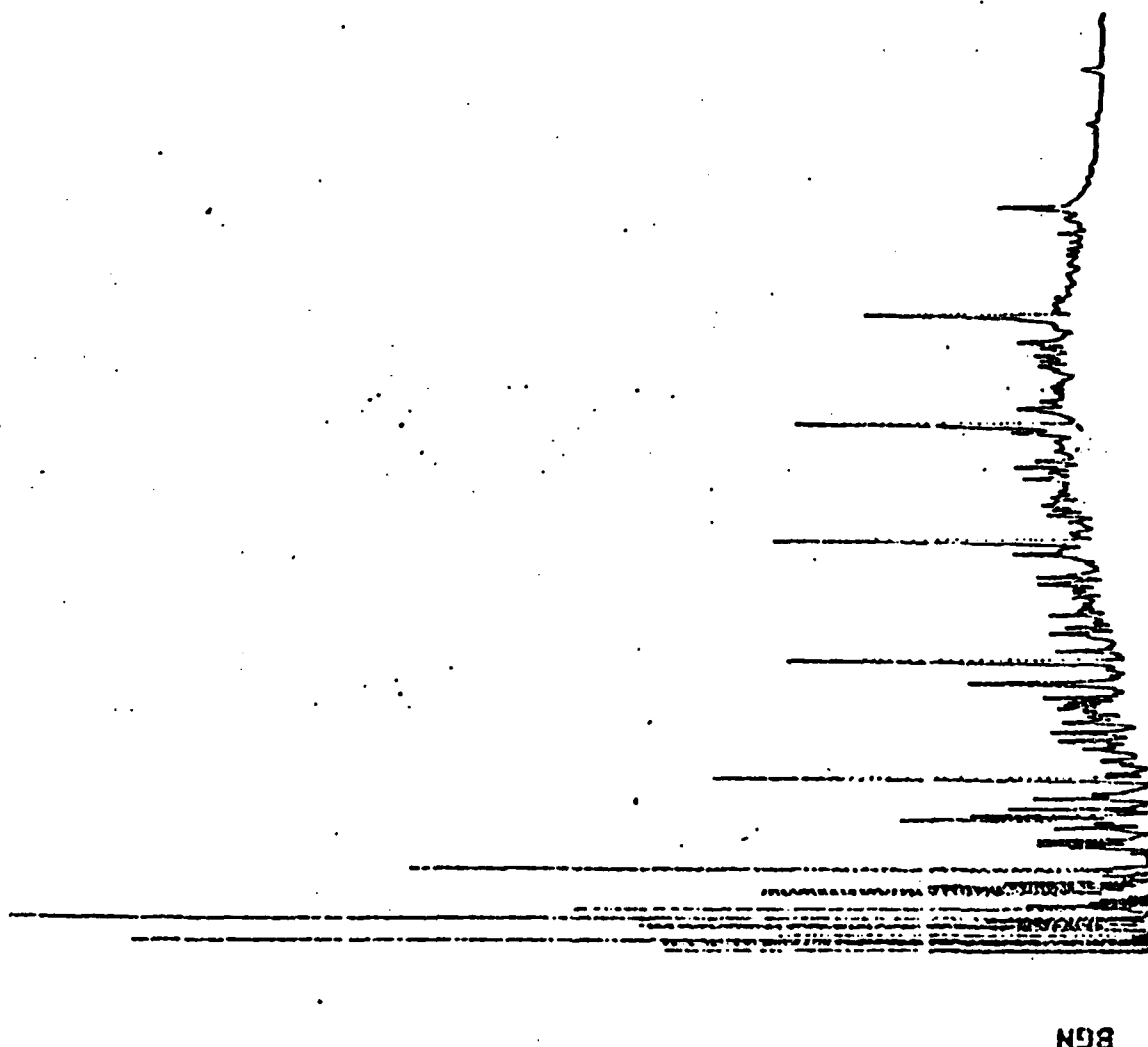


Fig. 4 - Avtag Gas Chromatogram

with the application of equipment to kerosene-type volatiles. The conditions employed were:-

Column: WCOT silica, coated with OV101
(methyl silicone)

Detection: FID @ 250°C

Injector Temperature: 250°C

Oven Program: 70°C for 5 minutes, 5 deg./min. to
150°C, 150°C for ∞

Split Ratio: 100:1

The chromatograms were considered satisfactory in reflecting differences in the volatilities of the three fuels.

Attempts were next made to determine the volatile contaminant contents of a number of used lubricant samples received from AFWAL. The scheme adopted was to add to the test sample a known amount of some substance which would serve the purpose of both an internal standard and marker so that the areas of the peaks eluting before the marker could be summed up and, after calibration, could be calculated against the area generated by the marker.

The use of a marker has merit in compensating variances from differences in equipment between different laboratories, but the choice of marker required careful consideration for, in the determination of VCC, it must represent the demarcation between volatile and non-volatile contaminants in accordance with the definition of VCC imposed by the reclamation technology and given in STM No. 1. However, candidate markers were initially selected from likely materials that happened to be available in the Dalton laboratory, the choice of the most suitable marker being left in abeyance pending the outcome of this exploratory work and finalisation of a satisfactory GLC methodology.

Using various markers and the GLC conditions with the OV101 column employed above for the turbine fuels, volatile materials in the used lubricant samples were eluted, followed by the marker, but the time taken afterwards to elute the lubricant was too long, even at increased oven temperatures, to achieve adequate cleaning of the column for subsequent use.

The column and other conditions were then changed to those below, and tests were run on a number of standards prepared by blending known amounts of Avtur turbine fuel ranging from one to ten percent with a polyol-ester base lubricant stock (Emolein 2939), and to each of which was added one percent 2-ethylhexanol (EH) as marker and internal standard.

Column: WCOT silica carbowax 20 M
(polyethyleneglycol)

Detection: FID @ 200°C

Injector Temperature: 200°C

Oven Program: 70°C for 5 minutes, rising to 130°C
@ 40 deg./min. Held @ 130°C for 5
minutes, then increased to 200°C @
40 deg./min., and held @ 200°C for
15 minutes.

Split Ratio: 100:1

Promising results were obtained initially but, after having performed a number of determinations, results calculated from subsequent determinations without renewing the column were at variance with the known concentrations of Avtur present, and did not seem reasonable upon visual inspection of the peak areas generated. The chromatograms at this stage were very noisy, and it became apparent that elution of the ester base-stock component of the standard was taking place.

The potentiality of the UV101 column was then re-investigated by reducing its length from 25 to 5 M. This was successful in lowering analysis time to about 30 minutes in tests run with Avtur turbine fuel as experimental contaminant, and qualitatively, promising chromatograms were obtained with n-tridecane as marker which was attractive in that its boiling point of 235.5°C lies in the neighbourhood of the demarcation between volatile and non-volatile contaminants as defined under 2.1 and in STM No. 1. Quantitatively, however, low results were obtained for Avtur contaminant when n-tridecane was utilised as the internal standard due, it was postulated, to the presence of n-tridecane or hydrocarbons of similar boiling point in the Avtur fuel.

Using the shorter OV101 column, but n-hexadecane as marker and internal standard, and by increasing oven programme temperatures, conditions were established at which the Avtur contaminant appeared in the chromatogram as one or a few peaks clearly divorced from the hexadecane peak which appeared a little later. Electronic integration of the "compressed" chromatogram obtained in this way was accurately accomplished in contrast with difficulties which were encountered in attempts to integrate the more "expanded" chromatogram illustrated in Fig. 2. Addition of n-tridecane (boiling point 235.5°C) to the Avtur contaminated lubricant was found to elute with the last three percent or so of the eluted Avtur hydrocarbons. This is consistent with the definition of VCC but, unlike hexadecane (boiling point 287°C), tridecane could not be adopted as the marker since it was not resolved from Avtur in the "compressed" chromatogram.

2.2.1.1 Application to Non-Hydrocarbon Volatile Contaminants

The method was next applied to unused turbine engine lubricant to which known amounts of possible non-hydrocarbon contaminants were added. The response factors, however, for contaminants such as trichlorethane, methanol and other alcohols for example were found to be nearer to 0.3 than to the response factor of 1.0 which was obtained for kerosene and other hydrocarbons, i.e., sufficiently low to rule out the feasibility of a GLC technique for determination of VCC in the generalised sense.

2.2.1.2 Scope of STM No. 2

It was decided in the light of the foregoing results to model STM No. 2 on the GLC conditions established for Avtur contaminant, and to limit the scope of the method to the determination of volatile hydrocarbon content in the absence of non-hydrocarbon volatile contaminants. Details of the finalised method are given in Appendix B in which volatile hydrocarbon content (VHC) is defined as those hydrocarbon contaminants which are more volatile than n-hexadecane boiling at 287°C.

Chromatograms obtained upon application of the method to aliquots of unused turbine engine lubricant coded ATL.9102* to which approximately one percent additions of Avtur, Avcat and Avtag kerosene type turbine fuels were made are illustrated in Figs. 5, 6 and 7 respectively. The reduced retention times in these chromatograms may be appreciated upon comparing them with those in Figs. 2, 3 and 4.

Results obtained upon application of the method, strictly in accordance with Appendix B, to the three standards employed in the assessment of STM No. 1 are presented in Table III in which are recapitulated for comparison the results furnished by STM No. 1.

It will be apparent from these results and the definitions of VCC and VHC in STM No. 1 and STM No. 2 respectively that in the absence of non-hydrocarbon volatile contaminants, results furnished by STM No. 2 for Avtur kerosene may be expected to be about $100/97 = 1.03$ times those furnished by STM No. 1. No significant differences would be expected between the results from both methods for hydrocarbons boiling below 240°C, whereas higher results may be expected from STM No. 2 for hydrocarbons boiling between 240 and 287°C.

* Supplied by AFWAL under Contract No. F.49620-79C-0073.

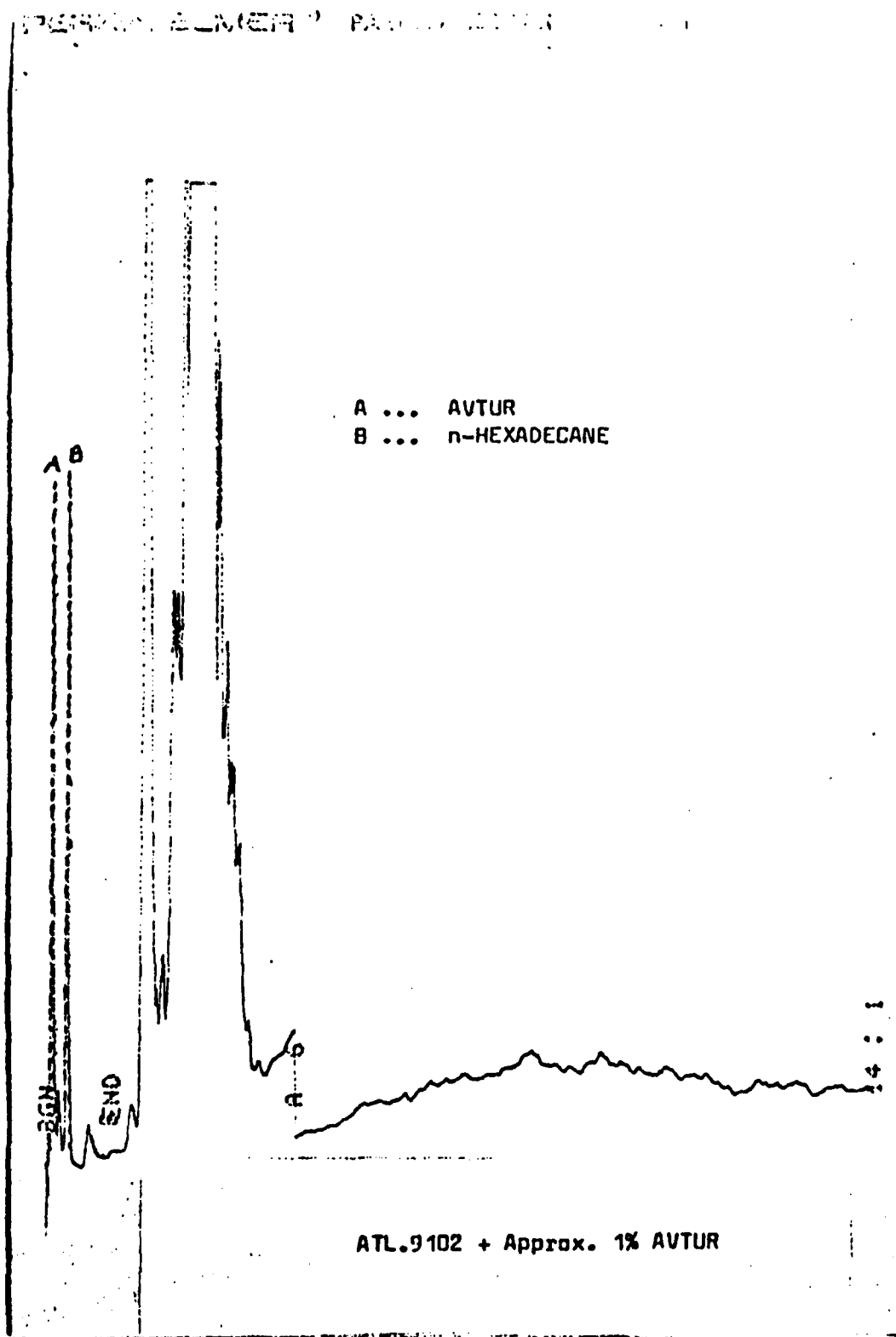


Fig. 5 - STM No. 2 Gas Chromatogram for Avtur Kerosene Contamination

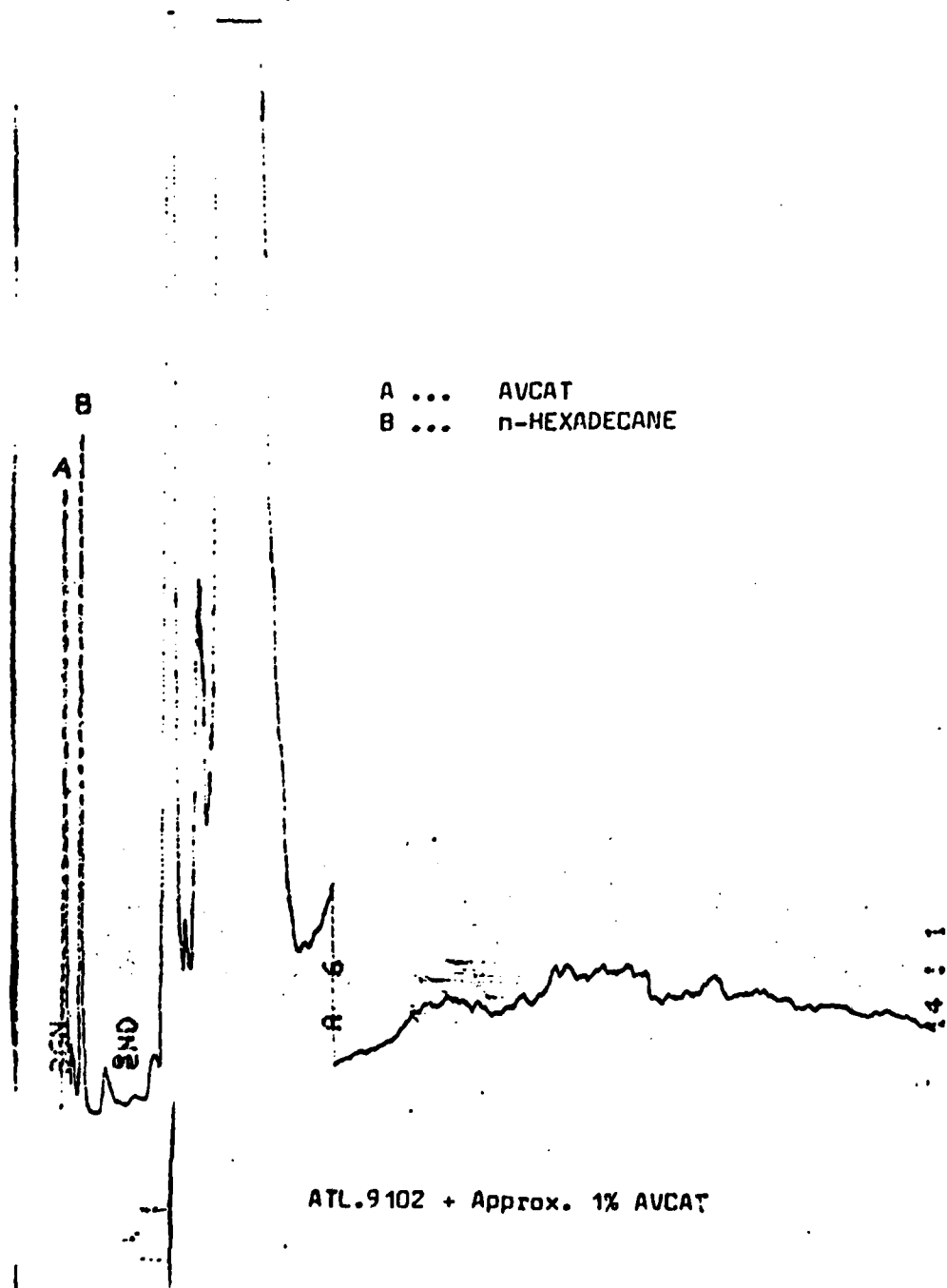


Fig. 6 - STM No.2 Gas Chromatogram for Avcat
Kerosene Contamination

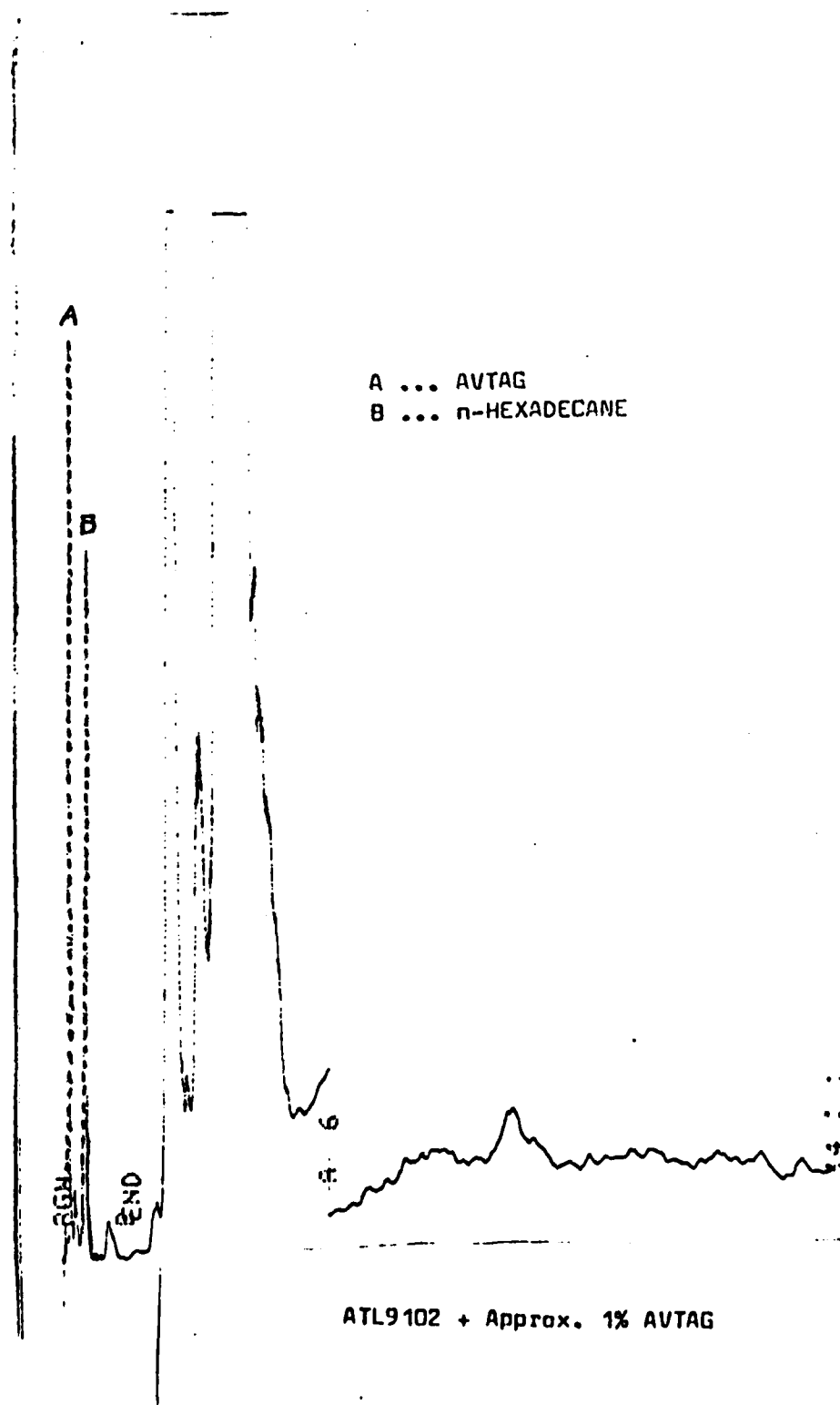


Fig. 7 - STM No.2 Gas Chromatogram for
Avtag Kerosene Contamination

TABLE III

Standard		VCC % w/w by STM No. 1	VHC % w/w by STM No. 2
Ref.	Avtur Content % w/w		
A	19.3	19.0	17
B	Nil	0.07	0.1
C	2.47	2.38	2.5

2.2.2 Discussion

Development of STM No. 2 had the original objective of screening out samples of used lubricant containing one percent or less of VCC in order to avoid the application of the more time consuming STM No. 1 to such samples. However, for the reasons explained above, it became necessary to limit the scope of the method to the determination of VHC in the absence of non-hydrocarbon volatile contaminants. Some lubricant samples may indeed contain non-hydrocarbon volatile contaminants, and it remains, therefore, to consider the effect of this upon the applicability of STM No. 2 to such samples.

Referring to 2.2.1.1, non-hydrocarbon volatile contaminants will increase the result obtained for VHC above the amount actually present, the presence of say, six percent trichloroethane increasing the result by two percent in terms of VHC. This, however, is of little concern for it would correctly place the sample in the group ($VCC > 1\%$) requiring application of STM No. 1 even if volatile hydrocarbons were absent.

Considering, on the other hand, used lubricant containing for example no volatile hydrocarbons but, say, two percent trichloroethane, the application of STM No. 2 would yield a result of 0.7 percent in terms of VHC, and thereby incorrectly place the lubricant in the group not subject to stripping by STM No. 1. Incorrect grouping in cases of this kind is, however, extremely improbable for quite small concentrations of non-hydrocarbon volatile contaminants give rise to abnormal odour which would dictate the application of STM No. 1, regardless of VHC, in accordance with the preliminary inspection scheme given later under 3.1.

2.3 STM No. 3 - Determination of Mineral Oil Content (MOC)

It has been the experience of Dalton in the reclamation of commercial arisings of ester-base turbine engine lubricants that the presence of not more than 5% mineral oil in the used lubricant, after removal of volatile contaminants, is acceptable in the reclaimed product whereas, depending upon the type of the mineral oil (non-volatile hydrocarbon contaminant) higher concentrations may impair the low-temperature fluidity of the product.

An assessment was made of each of four techniques, which are outlined below with the results obtained, for determination of mineral oil content.

2.3.1 Rolls-Royce Method 1014

This method, which depends upon the difference between the solubilities of ester-base lubricants and mineral oils in acetic acid solution, was known to produce, in the absence of

unsaponifiable components of the ester lubricant, satisfactory results for paraffinic mineral oil concentrations exceeding 5%, and a short excursion was, therefore, made into the applicability of the method to polyol-ester type MIL-L-7808 lubricant containing known concentrations of paraffinic and naphthenic mineral oils.

Reasonably satisfactory results were obtained in tests conducted with ATL.9100* to which 1 and 5% of a predominantly paraffinic oil had been added. Similar tests carried out with ATL.9100 to which two different, but predominantly naphthenic, mineral oils had been added, failed, however, to show the presence of either oil at 1% concentration, and less than half the amounts added at 5% concentration were found.

It was evident from these results that RR.1014 could not be relied upon for screening out lubricants containing more than 5% naphthenic type mineral oil from those containing 5% or less.

2.3.2 Solvent Extraction of Mineral Oil from Saponified Test Sample followed by Gravimetric Finish

The modus operandi followed in this technique is detailed in Appendix D. Briefly, polyols liberated by saponification are soluble in the aqueous phase of dissolved potassium salts, whereas the monohydric alcohols liberated from diester components of the lubricant, while insoluble in the aqueous phase, are soluble in diethyl ether, and, therefore, accompany mineral oil in the ethereal extract. The method makes use of the solubility of the liberated diester alcohol moiety and the insolubility of mineral oil, in ethanol which is employed for separating the one from the other in the dried ethereal extract.

A number of preliminary tests were run by applying the technique to a polyol-ester and dibasic ester lubricant to which known amounts of paraffinic and naphthenic oils had been added. Promising results were obtained initially, but later were found to be not all that repeatable.

The technique required manipulative skill in carrying it out, but suffered from the main disadvantage of being time consuming, 20 hours at least being necessary to complete the saponification step above. Also the life of the Erlenmeyer flask employed in this step was dramatically shortened by attack from the potassium hydroxide solution. Further assessment of the technique was abandoned since it soon became obvious that it would be unsuitable for routine purposes.

* Polyol-ester lubricant supplied by AFWAL under Contract No. F.49620-79C-0073.

2.3.3 Separation of Mineral Oil by Means of Sulphuric Acid

Sulphuric acid as a differential solvent was firstly investigated by carrying out tests on standards prepared by dissolving measured amounts of a predominantly naphthenic mineral oil in polyol ester turbine engine lubricant ATL.9100* to produce therein mineral oil concentrations of nil, 1, 2, 5, 10 and 90%.

The test on each standard was carried out by introducing 25 ml. sulphuric acid (sp. gr. = 1.8), followed by 10 ml. of the standard into a modified Babcock form of bottle** which was then swirled to mix the contents. The bottle and contents were cooled under running water, and sulphuric acid of the same strength as before was added to the uppermost graduation mark of the neck of the bottle which was then shaken for 5 minutes, with intermittent venting to relieve any pressure increase.

The bottle and contents were then centrifuged twice, each time for 15 minutes and, after 15 minutes standing, the contents were inspected for separation of mineral oil as a distinct phase surmounting the remainder of the contents which had assumed a dark-brown coloration, presumably due for the most part to oxidation of inhibitors.

The supernatant phase in all the tests was water-white in appearance, and the observed volumes, expressed as percent of test sample, are presented in Table IV where they are rounded off to the nearest 0.5% (one subdivision of the Babcock-type bottle represents 0.5% on the volume of the sample taken viz., 10 ml.).

The results are seen to range from 80 to 100% of the mineral oil contents of the standards employed, and to exhibit good repeatability in the four tests on the standard containing 5% by volume of mineral oil.

The test method was next applied to a diester turbine engine lubricant ATL.9101* to which a predominantly paraffinic mineral oil was added to produce standards containing 1, 5 and 10% mineral oil. The results are presented in Table V in which it is seen that clear water-white supernatant layers varying from 50 to 80% of the mineral oil contents of the standards were obtained.

* Supplied by AFWAL under Contract No. F.49620-79C-0073.

** Neck graduated in units from 0 to 10 over length of 65 mm., and subdivided in 0.1 units, each equivalent to 0.05 ml. Capacity of bottle to zero (lowest mark on neck) = 44.1 ml. Overall height and diameter of bottle = 190 mm. and 30 mm. respectively.

No observations were made in the foregoing tests of the effect of allowing the tested samples to stand longer than the 15 minutes following centrifuging, but, assuming the supernatant water-white layers of fluid did in fact consist exclusively of mineral oil, the results indicate that the test method, while not all that quantitative, might be useful as a semi-quantitative or qualitative test for mineral oil.

The possibility of this was, therefore, explored further by applying the test method to standards prepared by blending 2% by volume of a predominantly naphthenic mineral oil in each of three polyol ester lubricants viz., TEL.0027*, TEL.0028*, TEL.0029*, and two commercial base-stocks, one of which comprised a TMP-triester**, and the other DOS***. The method was applied also to a diester lubricant TEL.0026* to which no mineral oil was added, and to a blend comprising equal volumes of TEL.0028 and TEL.0026 containing 2% by volume of the mineral oil. Observations in these tests were made at the end of the 15 minutes standing in accordance with the method, and also at the end of a further standing period of seven days. The results are presented in Table VI in which it is seen that:-

- (a) The supernatant water-white layers from the polyol ester standards are of the right order of magnitude, and probably consist of mineral oil since no increase in volume occurred with extended standing period. However, the supernatant gel furnished by the TEL.0029 standard is obviously not mineral oil, but a decomposition product, and the method is, therefore, not applicable to all polyol ester lubricants, even for qualitative purposes.
- (b) The supernatant water-white layers from the diester lubricants cannot consist of mineral oil exclusively for none was present in the TEL.0026 standard, and the increase in volume which occurred upon extending the standing period, greatly exceeds the mineral oil content of the DOS standard. The relatively large volume of the separated material would appear to be a diester decomposition product, the diesters in general being less stable than the polyol esters.
- (c) The apparent instability of TEL.0026 towards concentrated sulphuric acid is manifested also in the behaviour of the TEL.0028/TEL.0026 blend containing the apparently stable polyol ester TEL.0028.

* Supplied by AFWAL under Contract No. F.49620-79C-0073.

** Unichema Chemie Product "Emolein 2934".

*** Ciba-Geigy product "Reolube DOS".

TABLE IV

Standard		Supernatant Layer % v/v
Ester	MOC % v/v	
Polyol Ester Lube AIL.9100	Nil	Nil
	1	1
	2	2
	5	4.4.4.4 (Repeat Tests)
	10	8.5
	90	7.5

TABLE V

Standard		Supernatant Layer % v/v
Ester	MOC % v/v	
Diester Lube ATL 9101	1	0.5
	5	4
	10	8

TABLE VI

Standard	MOC % v/v	Supernatant Layer		
		% v/v at end of:-		Appearance at end of 7 days standing
		15 minutes standing	7 days standing	
Ester				
Polyol Ester Lube TEL.0027	2	1.5	1.5	Clear, Water-White
Polyol Ester Lube TEL.0028	2	2	2	Clear, Water-White
Polyol Ester Lube TEL.0029	2	3.5	8	Light-Brown Gel
TMP-Triester Base-Stock	2	1.5	1.5	Clear, Water-White
Diester Lube TEL.0026	Nil	1	20	Clear, Water-White
DOS Base-Stock	2	2	20	Clear, Water-White
50/50 v/v TEL.0028/TEL.0026	2	2.5	15	Clear, Water-White, Surface Gelatinous

Following these unsatisfactory results, tests were carried out on the TEL.0029 and TEL.0026 standards in which the initial acid/sample ratio was varied from 0.5 to 4.0, but the results differed, but little, from those obtained at the original ratio of 2.5.

Finally, a few tests were carried out at the original ratio of 2.5, but with lower strength acid, again with unsatisfactory results.

2.3.4 Rolls-Royce Method 1032

This method utilises thin layer chromatography (TLC) for the determination of mineral oil and other materials in ester-base turbine engine lubricants, and provides specific test conditions for the determination of each material falling within the scope of the method.

Consistent results have been experienced by Dalton in the application of the method to used diester and polyol ester lubricants containing 5% or more of mineral oil after removal of volatile contaminants, the results obtained including any residual higher-boiling fractions from kerosene contaminant. Unsatisfactory results have been experienced, however, with mineral oil contents below about 3% which frequently, but not always, were not discernible at all as reaction spots on the chromatogram.

The cause of this capricious behaviour is not understood in spite of attempts that were made to elucidate the phenomenon by investigating the influence of technique variance. In contrast, no difficulties have been encountered by Dalton in applying the method to phosphate ester type hydraulic fluids containing as little as 0.1% mineral oil, the reaction spots for which were always clearly visible and repeatable.

A re-assessment of the method was made by applying it to ATL.9100* into which paraffinic and naphthenic mineral oils were introduced in concentrations ranging from 1 to 6%. The method was found to be suitable for determining mineral oil contents above 3%, but for lower concentrations it was found to be unreliable, especially for routine purposes where adherence to test details may not be all that rigorous.

2.3.5 Conclusion

RR Method 1032 was concluded to be suitable for screening out used ester-type turbine engine lubricants

* Polyol-ester lubricant supplied by AFWAL under Contract No. F.49620-79C-0073.

containing more than 5% mineral oil from those containing 5% or less. The method was, therefore, adopted as the basis of STM No. 3 given in Appendix C, but which is restricted in scope to the determination of mineral oil concentrations greater than 3% w/w.

3. Minimum Quality Specification

The first point to be clarified in considering development of a minimum quality specification for assessing the reclaimability of used turbine engine lubricant is the definition of the term reclaimability. This will obviously depend upon the particular specification which the reclaimed material is required to meet. The latter, in accordance with the scope of the present research, comprised MIL-L-7808 covering the USAF requirements for virgin lubricant.

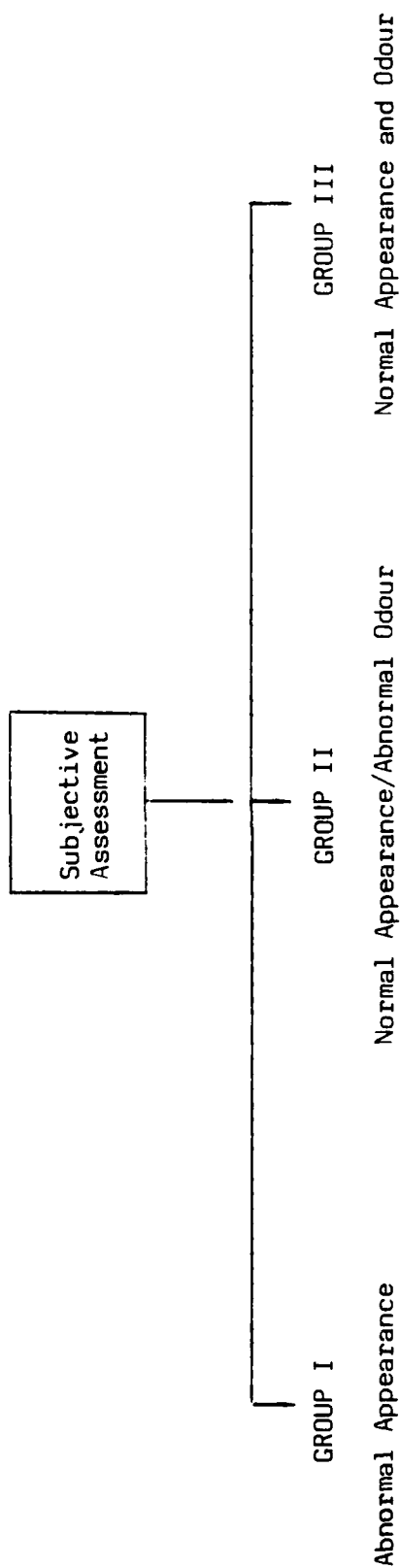
The second point is that whereas the minimum quality specification envisaged should employ test procedures which are readily carried out in the Laboratory, some of the requirements of MIL-L-7808 are in terms of lubricant behaviour which cannot be predicted from analytical or glassware-type tests, or even explained in terms of established lubricant concepts. If this were not the case, there would be no need, of course, to adopt such an elaborate specification.

The assessment of reclaimability by means of a simpler specification must, therefore, fall short of perfection for it cannot be expected to determine unequivocally whether or not a consignment of potentially reclaimable lubricant will conform, after reclamation by any technology, to every requirement of MIL-L-7808. This is particularly so when the used lubricant may have been contaminated during its collection and storage by unspecified materials foreign to the engine environment.

However, by taking advantage of experience acquired by Dalton in the inspection and reclamation of commercial arisings of synthetic turbine engine lubricants, and introducing where relevant modifications that were considered appropriate in extending this to MIL-L-7808 type arisings, a reasonably realistic minimum quality specification was formulated. This comprises the two inspection schemes explained below under 3.1 and 3.2.

3.1 Minimum Quality Preliminary Inspection (MQPI)

The MQPI scheme comprises the screening procedures outlined diagrammatically in Figs. 8, 9, 10 and 11. Lubricant samples are firstly screened subjectively into one or more of the three groups shown in Fig. 8, and those in each group are then examined in accordance with the procedure given for the appropriate group in either Fig. 9, 10 or 11. This has the ultimate effect of divorcing samples which are revealed at this stage to be definitely



NOTE: Kerosene odour and/or appearance of free-water not regarded as abnormal in application of the above scheme.

Fig. 8 - Minimum Quality Preliminary Inspection (MQPI) Groups

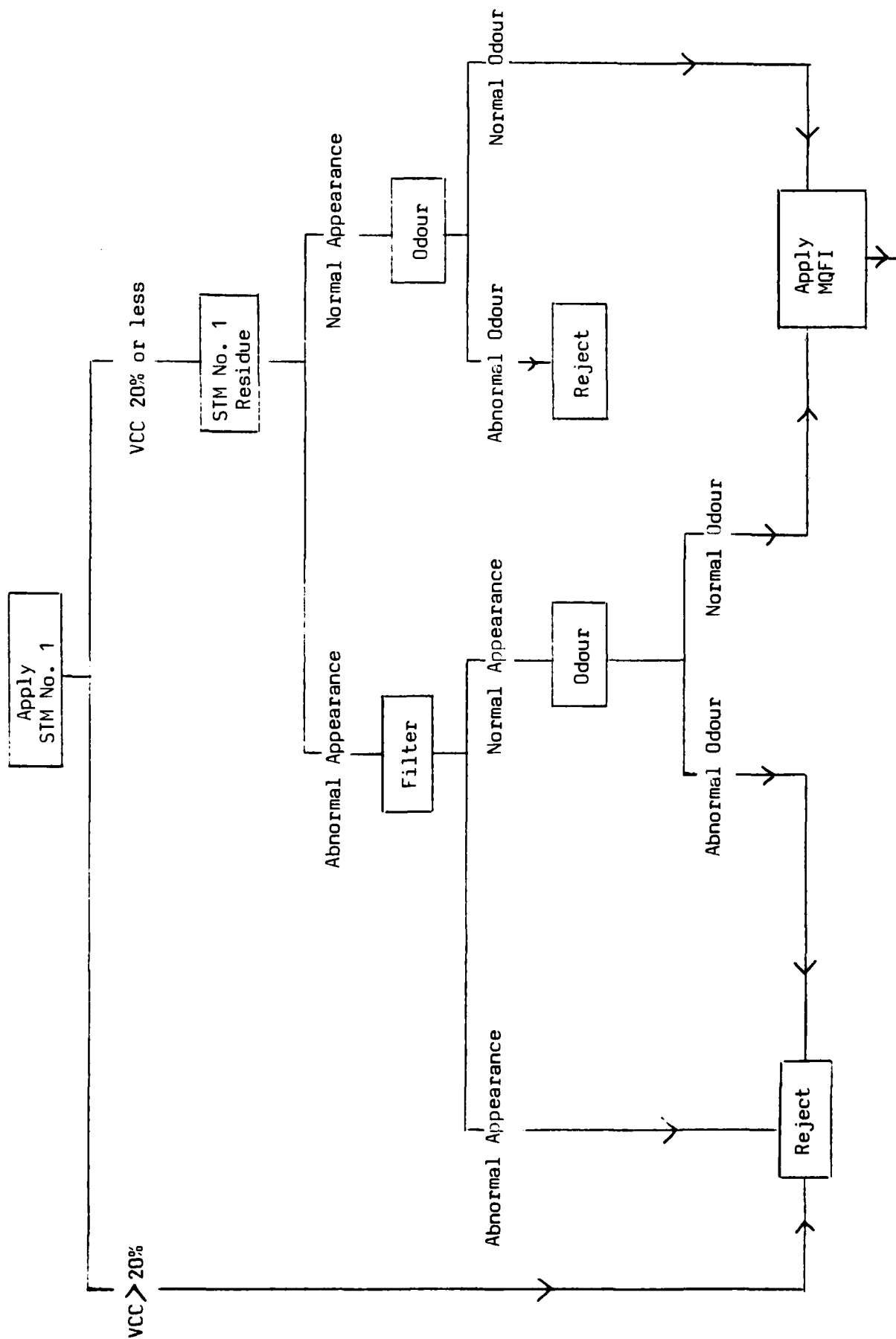


Fig. 9 - MQPI Group I: Abnormal Appearance

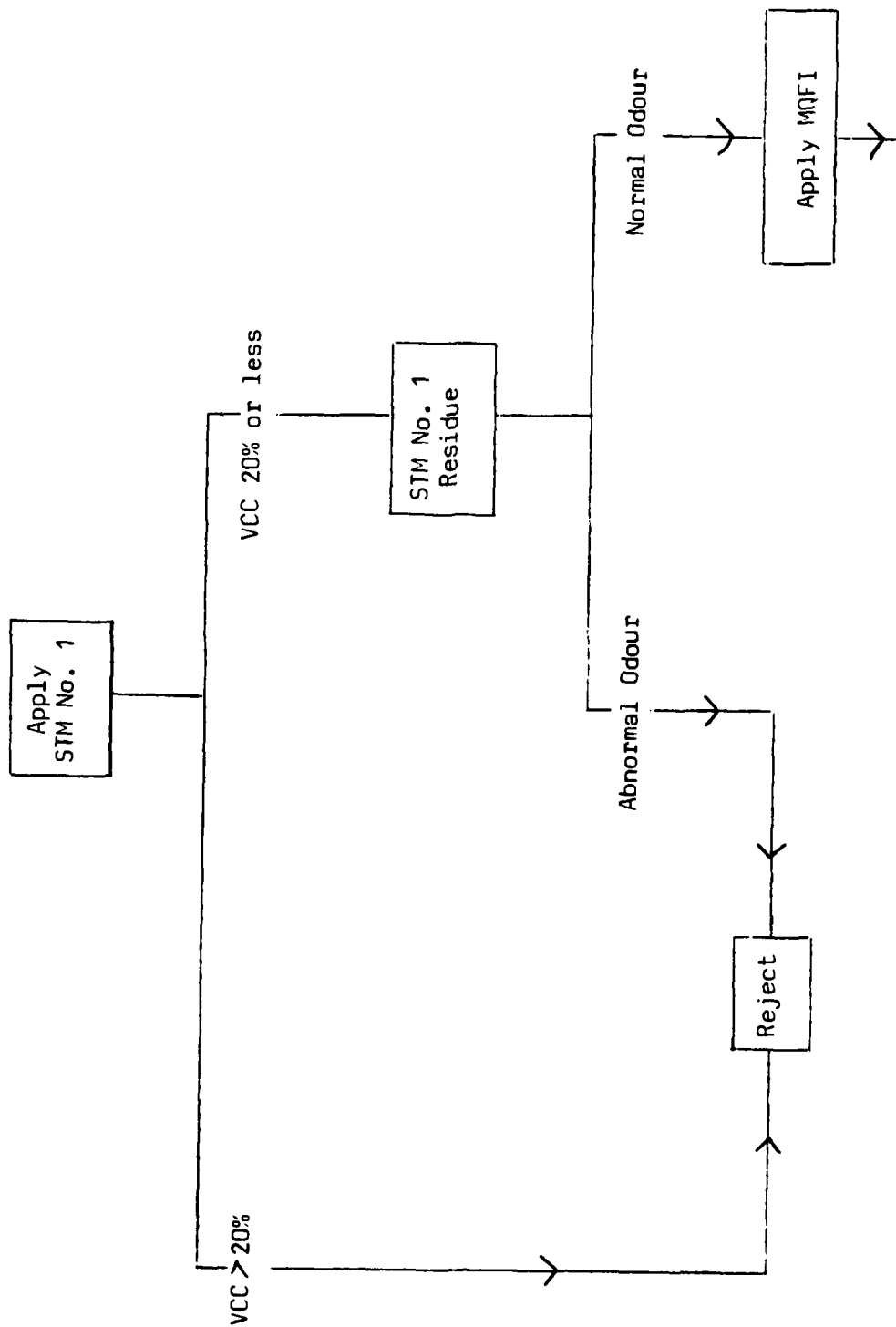


Fig. 10 - MQPI Group II: Normal Appearance/Abnormal Odour

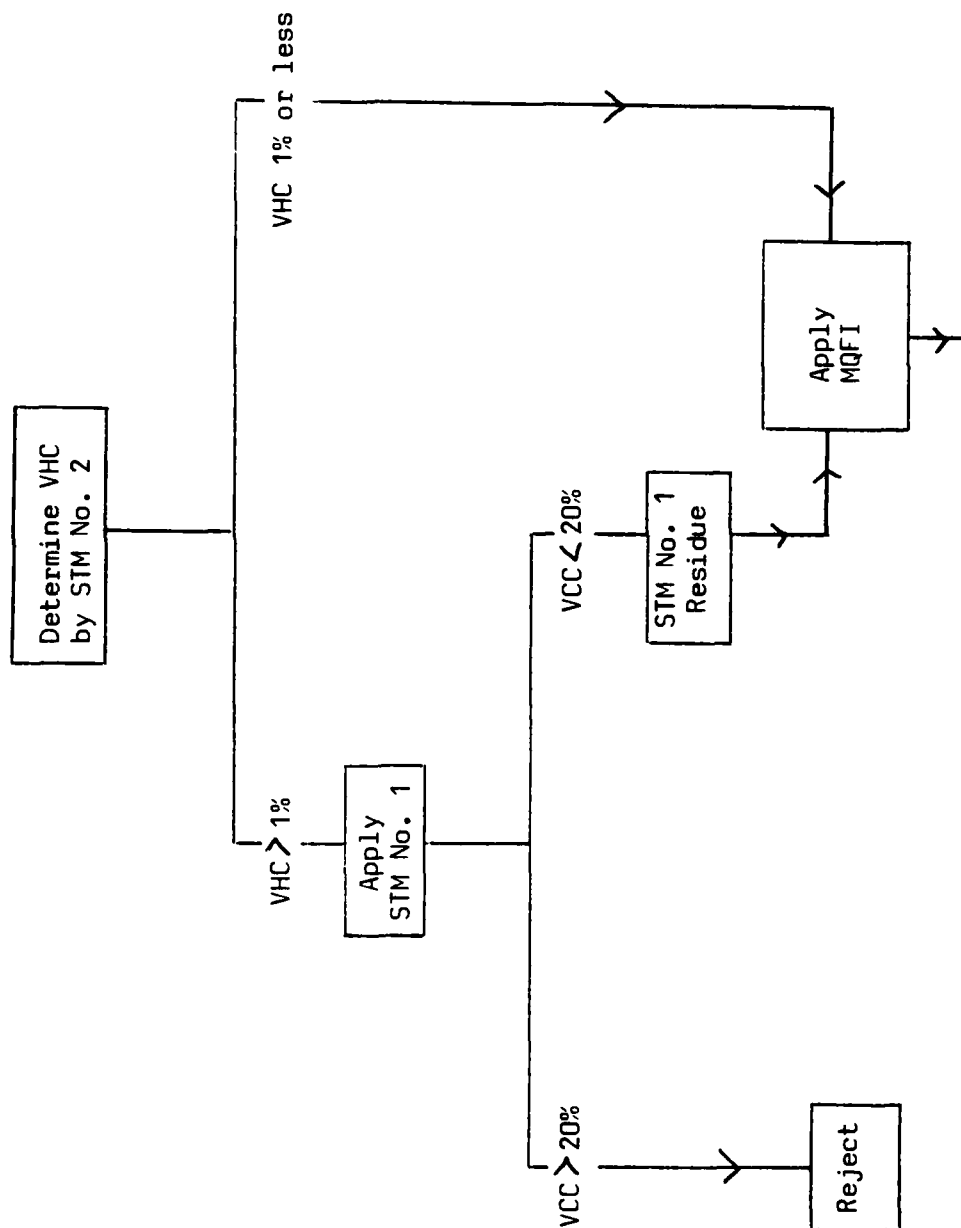


Fig. 11 - MQPI Group III: Normal Appearance and Odour

unreclaimable from those which are sufficiently promising to justify further attention by application of the MQFI scheme.

The tests involved in carrying out the MQPI, and the scope of the latter, may be summarised as follows:-

3.1.1 Tests

- (a) Subjective assessment of odour and appearance.
- (b) Determination of VHC.
- (c) Determination of VCC.
- (d) Filtration

3.2.2 Scope

Preliminary inspection serves the purpose of screening out collections of used lubricant which are unsuitable for reclamation by the Dalton technology on account of one or more of the following manifestations:-

- (a) VCC > 20% (technically but uneconomically reclaimable).
- (b) Abnormal appearance from contaminants which cannot be removed by the reclamation technology.
- (c) Abnormal odour from contaminants which cannot be removed by the reclamation technology.

3.2 Minimum Quality Final Inspection (MQFI)

3.2.1 Preliminary Considerations

The MQFI scheme explained below comprises a more critical screening procedure intended to be carried out on those consignments of used lubricant which the MQPI has indicated to be provisionally acceptable for reclamation. The objective is to divide such consignments into specific categories so that those in any one category differ less among themselves - in respect of the particular property or characteristic and magnitude thereof defining the category - than between those in different categories.

When a large background of experience exists, such as is the case with Rolls-Royce turbine engine lubricant arisings for example, a final inspection scheme will have been evolved which divides the consignments into two categories only. One of these, designated "reject", comprises consignments which can be said with 100 percent certainty are technically and/or economically unreclaimable. The other, spoken of as the "probably reclaimable" category, comprises consignments which, on average, can be said with a confidence of at least 99 percent, will satisfy the relevant specification after application of the Dalton technology; the proportion of consignments falling into this category from Rolls-Royce turbine engines is of the order of 95% when collected in accordance with a special scheme devised and implemented by Dalton.

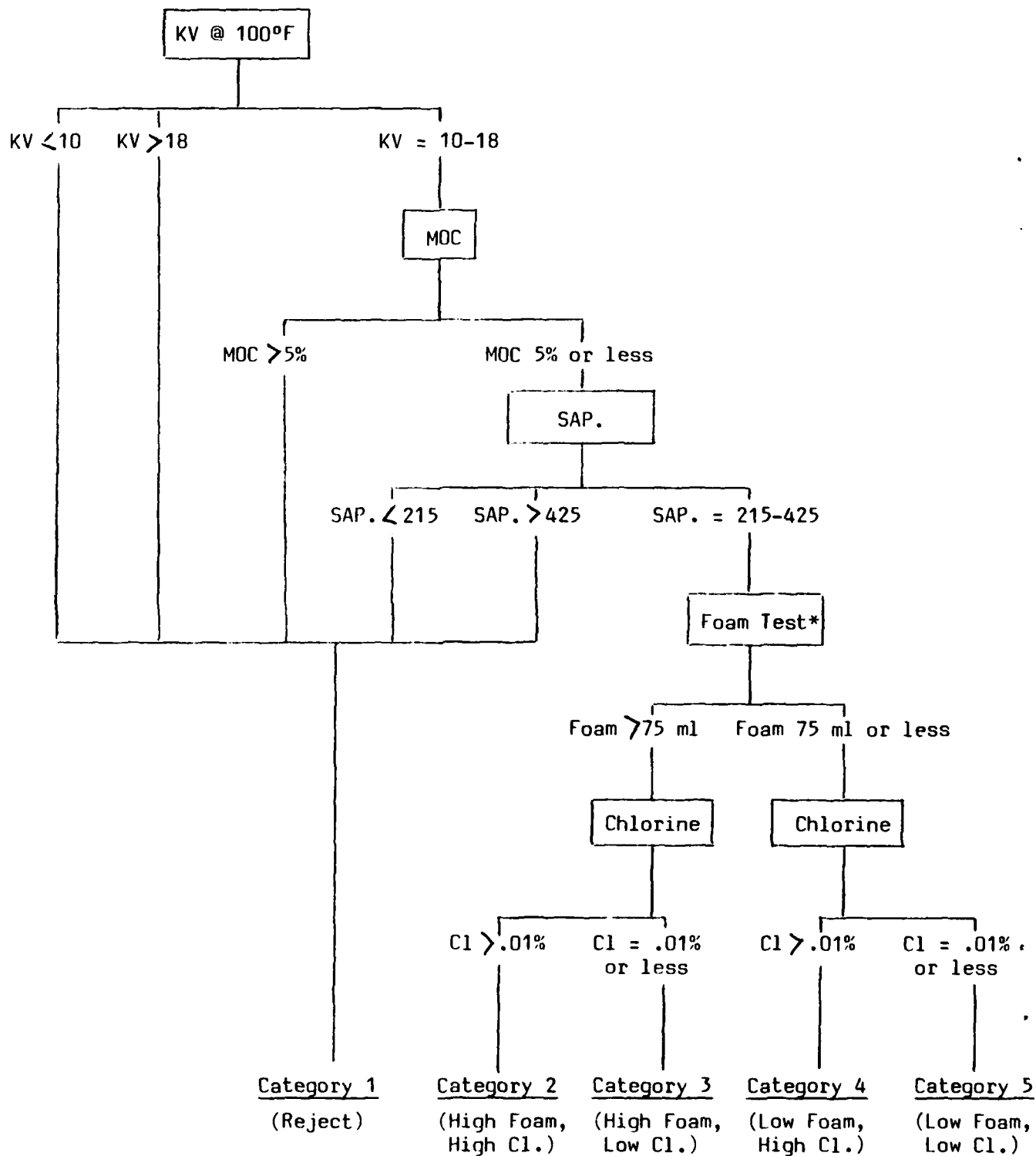
When but little experience exists, such as is at present the situation on the reclamation of USAF arisings, inclusion in the final inspection scheme of intermediate categories is warranted in the interest of resolving and utilising the maximum proportion of reclaimable consignments possible. The interim role of an intermediate category is to divorce from the above mentioned two main categories "borderline" consignments exhibiting some common contentious feature which can be resolved only by carrying out a reclamation exercise on that category.

An intermediate category of consignments found to be unreclaimable may often be utilised by blending them with sufficient consignments from the "probably reclaimable" category, but on the other hand, the latter could be ruined by blending in the wrong choice or proportions of intermediate consignments. No hard and fast rule can be laid down, and the blending of different categories of consignments is best left to the discretion and experience of the Reclaimer as might be specified by introducing an "Optional" clause to this effect in the specification for the reclaimed product.

3.2.2 MQFI Scheme

The MQFI screening procedure is outlined diagrammatically in Fig. 12 in which it is seen that the scheme screens the sample in the order of viscosity, MOC, saponification value, foaming propensity and chlorine content, and that it places the consignment represented by the sample into one of five categories.

Two of these are the main categories viz., "reject" and "probably reclaimable", and the remaining three, which are intermediate, are based upon foaming propensity and chlorine



* Foam volume in accordance with FED. STD. 991, Method 2313

Fig 12 - Minimum Quality Final Inspection (MQFI)

content. Using the notation of categories in Fig. 1, a consignment may be considered to be less contentious the higher the number of the category in which it is placed by the inspection results.

The highest confidence in the reclaimability of a batch of used lubricant consignments will thus be for those in Category 5, but this cannot be expected in the early application of the technology to USAF arisings to be as high as the confidence level of 99 percent mentioned earlier for Rolls-Royce arisings when consideration is given to the fact that some requirements of MIL-L-7808 are in terms of lubricant behaviour which cannot be predicted from used lubricant analysis or simple lubricant tests. The level of confidence can be expected to increase, however, and the number of intermediate categories in subsequent issues of the minimum quality specification to decrease, as experience in the reclamation of USAF arisings builds up.

4. Used Lubricant Samples

Seventy-one coded samples of used lubricant were received in all. The approximate sizes of the samples, and the bimonthly reporting period during which they arrived at the Dalton Refinery are given in Table VII; four of the samples were collected in the UK by EOARD, and were delivered in unmarked plastic containers which were subsequently designated by Dalton as Containers 1, 2, 3 and 4.

The samples totalled approximately 1103.5 kg in weight which, assuming an average specific gravity of 0.955, is equivalent to approximately 1155 litres or 305 US gallons, i.e. sufficient for compliance with Section B, item 4.1, page 3 of 11 pages of the contract.

4.1 Application of MQPI

The distribution of samples among the three groups of the MQPI were found to be as presented in Fig. 13. Twenty-two of the samples are seen to fall into Group I, three in Group II and forty-six in Group III. The odours and appearances dictating this distribution are recorded in Tables VIII, IX and X; the appearances of the samples were adjudged by placing aliquots in 250 ml. measuring cylinders and viewing them diametrically by transmitted and reflected daylight.

The samples in each group were next examined in accordance with the remainder of the appropriate MQPI scheme in Fig. 9, 10 or 11. The results obtained were as follows:-

4.1.1 MQPI Group I Samples - Abnormal Appearance

The abnormal appearance of ML0-81-144 was suggestive of

TABLE VII

Used Lubricant Samples Received by Dalton

Lubricant	Approximate Weight - kg	Samples Received During Bimonthly Period Ending:-
OP-232-1	13	81 June 30
OP-232-2	15	81 June 30
OP-232-3	8	81 June 30
OP-232-4	18	81 June 30
OP-232-5	14	81 June 30
OP-232-6	18	81 June 30
OP-232-7	15	81 June 30
OP-232-8	18	81 June 30
OP-232-9	17	81 June 30
OP-232-10	16	81 June 30
OP-232-11	18	81 June 30
OP-232-12	17	81 June 30
OP-232-13	16	81 June 30
OP-232-14	15	81 June 30
OP-232-15	13	81 June 30
OP-232-16	17	81 June 30
OP-232-17	17	81 June 30
OP-232-18	18	81 August 31
OP-232-19	18	81 August 31
OP-232-20	16	81 August 31
MLO-81-144	18	81 August 31
OP-232-21	17	81 August 31
OP-232-22	16	81 August 31
OP-232-23	18	81 August 31
OP-232-24	16	81 October 31
OP-232-25	16	81 October 31
OP-232-26	11	81 December 31
OP-232-27	18	81 December 31
OP-232-28	17	81 December 31

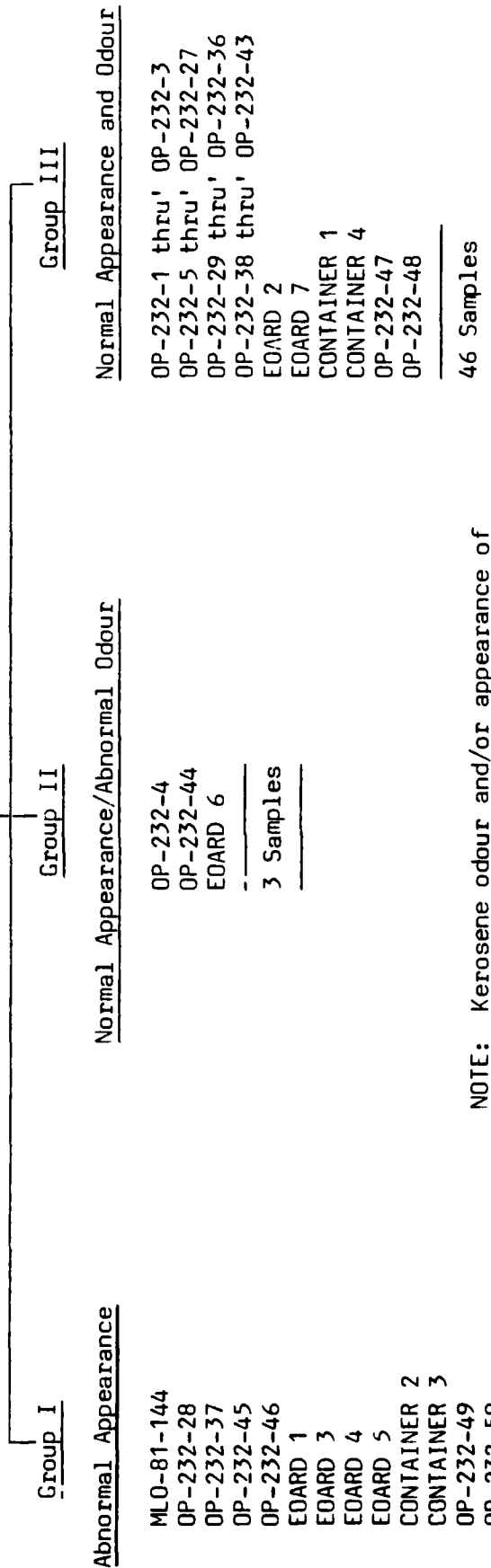
TABLE VII (continued)

Lubricant	Approximate Weight - kg	Samples Received During Bimonthly Period Ending:-
OP-232-29	15	81 December 31
OP-232-30	17	81 December 31
OP-232-31	19	81 December 31
OP-232-32	10	81 December 31
OP-232-33	14	81 December 31
OP-232-34	14	81 December 31
OP-232-35	16	81 December 31
OP-232-36	17	81 December 31
OP-232-37	17	81 December 31
OP-232-38	16	81 December 31
OP-232-39	16	81 December 31
OP-232-40	17	81 December 31
OP-232-41	15	81 December 31
OP-232-42	16	81 December 31
OP-232-43	13	82 February 28
OP-232-44	14	82 February 28
OP-232-45	18	82 June 30
OP-232-46	19	82 June 30
EOARD 1	16½	82 June 30
EOARD 2	19	82 June 30
EOARD 3	18	82 June 30
EOARD 4	16	82 June 30
EOARD 5	18	82 June 30
EOARD 6	15	82 June 30
EOARD 7	15	32 June 30
CONTAINER 1	3	82 August 31
CONTAINER 2	4½	82 August 31
CONTAINER 3	4½	82 August 31
CONTAINER 4	9	82 August 31
OP-232-47	17	82 August 31
OP-232-48	17	82 August 31
OP-232-49	17	82 August 31

TABLE VII (continued)

Lubricant	Approximate Weight - kg	Samples Received During Bimonthly Period Ending:-
OP-232-50	17	82 August 31
OP-232-51	18	82 August 31
OP-232-52	17	82 August 31
OP-232-53	17	82 August 31
OP-232-54	17	82 August 31
OP-232-55	15	82 August 31
OP-232-56	17	82 August 31
OP-232-57	16	82 August 31
OP-232-58	19	82 August 31
OP-232-59	14	82 October 31

Subjective
Assessment



NOTE: Kerosene odour and/or appearance of free-water not regarded as abnormal in application of the above scheme

Fig. 13 - Minimum Quality Preliminary Inspection (MQPI)
Subjective Grouping of Used Lubricant Samples

TABLE VIII

MQPI Group I Samples - Abnormal Appearance

Sample	Odour	Appearance
MLO-81-144	-	Bright Red/Clear
OP-232-28	Slight Kerosene	Slightly Cloudy/ Pale Amber
OP-232-37	Kerosene	Cloudy/Amber Red
OP-232-45	Kerosene	Slightly Cloudy/ Amber Red
OP-232-46	Kerosene	Cloudy/Amber Red
EOARD 1	-	Black
EOARD 3	Kerosene	Cloudy/Amber Brown
EOARD 4	Chlorinated Solvent	Black
EOARD 5	Not Recognisable	Cloudy/Amber Brown
CONTAINER 2	Normal	Amber Red/Cloudy
CONTAINER 3	Normal	Pale Amber/Cloudy
OP-232-49	Kerosene	Pale Amber/Slightly Cloudy
OP-232-50	Kerosene	Amber Red/Slightly Cloudy
OP-232-51	Kerosene	Dark Brown/Cloudy
OP-232-52	Kerosene	Dark Brown/Cloudy
OP-232-53	Kerosene	Amber Brown/Cloudy
OP-232-54	Kerosene	Amber Brown/Cloudy
OP-232-55	Kerosene	Pale Amber/Cloudy
OP-232-56	Chlorinated Solvent	Pale Amber/Cloudy
OP-232-57	Kerosene	Amber Red/Cloudy
OP-232-58	Kerosene/ Chlorinated Solvent	Amber Red/Cloudy
OP-232-59	Kerosene	Cloudy/Amber Red

TABLE IX

MQPI Group II Samples - Normal Appearance/Abnormal Odour

Sample	Odour	Appearance
OP-232-4	Slightly Phenolic	Normal/Dark Red- Brown
OP-232-44	Faintly Sweet	Normal/Amber Red
EOARD 6	Sweet	Normal/Amber Brown

TABLE X

MQPI Group III Samples - Normal Appearance and Odour

Sample	Odour	Appearance
OP-232-1	Normal	Normal/Amber Red
OP-232-2	Normal	Normal/Pale Amber
OP-232-3	Normal	Normal/Pale Amber
OP-232-5	Normal	Normal/Dark Red-Brown
OP-232-6	Normal	Wet/Amber Red
OP-232-7	Normal	Normal/Amber Red
OP-232-8	Normal	Wet/Amber Red
OP-232-9	Normal	Wet/Amber Red
OP-232-10	Normal	Normal/Amber Red
OP-232-11	Normal	Wet/Amber Red
OP-232-12	Normal	Wet/Amber Red
OP-232-13	Kerosene	Approx. 80% Water
OP-232-14	Kerosene	Normal/Pale Amber
OP-232-15	Normal	Normal/Pale Amber
OP-232-16	Normal	Normal Pale Amber
OP-232-17	Normal	Normal/Pale Amber
OP-232-18	Normal	Normal/Amber Red
OP-232-19	Normal	Normal/Pale Amber
OP-232-20	Normal	Normal/Pale Amber
OP-232-21	Normal	Normal/Pale Amber
OP-232-22	Normal	Normal/Amber Brown
OP-232-23	Normal	Normal/Amber Brown
OP-232-24	Normal	Wet/Amber Red
OP-232-25	Kerosene	Normal/Pale Amber
OP-232-26	Normal	Normal/Dark Amber
OP-232-27	Normal	Normal/Amber Red
OP-232-29	Normal	Normal/Amber Brown
OP-232-30	Normal	Normal/Amber Red
OP-232-31	Normal	Normal/Amber Red
OP-232-32	Normal	Normal/Pale Amber

TABLE X (continued)

Sample	Odour	Appearance
OP-232-33	Normal	Normal/Amber Brown
OP-232-34	Normal	Normal/Dark Amber
OP-232-35	Kerosene	Normal/Amber Brown
OP-232-36	Kerosene	Normal/Amber Red
OP-232-38	Kerosene	Normal/Amber Brown
OP-232-39	Kerosene	Normal/Amber Red
OP-232-40	Kerosene	Normal/Amber Red
OP-232-41	Kerosene	Normal/Pale Amber
OP-232-42	Kerosene	Normal/Amber Red
OP-232-43	Normal	Cloudy/Dark Amber
EOARD 2	Normal	Normal/Amber Red
EOARD 7	Normal	Normal/Dark Amber
CONTAINER 1	Kerosene	Pale Amber/Clear
CONTAINER 4	Slight Kerosene	Pale Amber/Clear
OP-232-47	Kerosene	Dark Brown/Clear
OP-232-48	Kerosene	Dark Brown/Clear

a petroleum-base hydraulic fluid, and certainly not synthetic turbine engine lubricant. This sample was not, therefore, examined in accordance with the scheme in Fig. 9 for screening Group I samples, but was rejected at this stage as unreclaimable.

Referring to Fig. 9, the VCC results, and the appearances and odours of the remaining samples after removal of VCC by means of STM No. 1, are presented in Table XI, in which are brought forward from Table VIII for convenient comparison the appearances and odours of the samples before removal of VCC.

The volatile contaminant contents of all but one of the samples are seen to range from 0.8 to 20% which are not outside the acceptance limit for VCC in Fig. 9. The remaining sample viz., OP-232-59 is seen to contain as much as 36% VCC which greatly exceeds the acceptable maximum of 20%, and which was, therefore, sufficient cause for rejection of the sample at this stage of the inspection.

The appearances and odours of fifteen of the samples are seen to have become normal upon the removal of VCC. These, except OP-232-59, were, therefore, released for MQFI.

The abnormal appearances of the remaining six samples are seen to have persisted after removal of VCC, and these were, therefore, next screened by filtration in accordance with Fig. 9. The filtration technique employed is given in Appendix E, and the results obtained are presented in Table XII. It is seen that the appearances and odours of five of these samples were satisfactory after filtration, and they were, therefore, released for MQFI. The black appearance of EOARD 1, however, remained unaltered after filtration, and this sample was, therefore, rejected as unreclaimable.

4.1.1.1 MQPI Group I Samples Rejected as Unreclaimable

It is seen that three of the twenty-two Group I samples were rejected as unreclaimable. No further examination of these rejected samples was necessary in the application of the MQPI but, as a matter of interest, they were in fact examined further as below:-

MLO-81-144

Infra-red spectroscopy indicated this sample to consist almost entirely of MIL-H-5606B hydraulic fluid, and determination of its saponification value yielded a result of 9 mgKOH/g which would be accounted by postulating the presence of about 3% ester type turbine engine lubricant.

EOARD 1

Test data obtained for this sample after removal of VCC

are presented in Table XIII in which are also presented results obtained for OP-232-59.

The results for EOARD 1 indicate that the sample had been taken from MIL-L-23699 arisings excessively contaminated by mineral oil. It is evident that had the sample not been rejected by MQPI, it would have been rejected subsequently by MQFI (Fig. 12) on account of high viscosity and excessive MOC.

OP-232-59

This sample had been rejected by MQPI on account of excessive VCC as already explained. It is evident from Table XIII that had the sample not been rejected at this stage, it would have been rejected subsequently by MQFI on account of high viscosity and excessive MOC. The results indicate that the sample had been taken from MIL-L-23699 arisings excessively contaminated by mineral oil and turbine engine fuel hydrocarbons.

4.1.2 MQPI Group II Samples - Normal Appearance/Abnormal Odour

Referring to Fig. 10, the VCC results and the odours of the three samples in this group after removal of VCC by means of STM No. 1 are presented in Table XIV, in which are brought forward from Table IX for convenient comparison the odours of the samples before removal of VCC.

The volatile contaminant contents of the samples are seen to range from 1.3 to 6.4% which are not outside the acceptance limit for VCC in Fig. 10, and the odours of all three samples are seen to have become normal upon the removal of VCC. These samples were, therefore, released for MQFI.

4.1.3 MQPI Group III Samples - Normal Appearance and Odour

OP-232-13 in this group was rejected by visual examination only since it was observed to contain more than 80% free water, the small lubricant content of which would not be worth reclaiming.

The remaining forty-five samples in the group were firstly screened in accordance with Fig. 11 by determining their volatile hydrocarbon contents by means of STM No. 2, the results for which are presented in Table XV. It is seen that twenty-eight of these samples contained less than 1% and seventeen contained more than 1% VCC.

4.1.3.1 Samples Containing Less Than 1% VCC

These were released for MQFI in accordance with Fig. 11.

TABLE XI

Volatile Contaminant Contents of MQPI Group I Samples, And The Effect of Removing
VCC Upon Odour And Appearance

Sample	Appearance		Odour		VCC % w/w
	Before Removal of VCC*	After Removal of VCC	Before Removal of VCC*	After Removal of VCC	
ML0-81-144	Bright Red/Clear	-	-	-	-
OP-232-28	Cloudy/Pale Amber	Clear/Normal	Slight Kerosene	Normal	2.8
OP-232-37	Cloudy/Amber Red	Clear/Normal	Kerosene	Normal	10
OP-232-45	Cloudy/Amber Red	Clear/Normal	Kerosene	Normal	5.0
OP-232-46	Cloudy/Amber Red	Clear/Normal	Kerosene	Normal	5.3
EOARD 1	Black	N.C.	Normal	-	0.8
EOARD 3	Cloudy/Amber Red	Clear/Normal	Kerosene	Normal	5.8
EOARD 4	Black	Clear/Normal	Chlorinated Solvent	Normal	1.0
EOARD 5	Cloudy/Amber Red	N.C.	Unrecognisable	-	8.1
CONTAINER 2	Cloudy/Amber Red	Clear/Normal	Normal	Normal	1.9
CONTAINER 3	Cloudy/Pale Amber	Clear/Normal	Normal	Normal	4.1
OP-232-49	Cloudy/Pale Amber	N.C.	Kerosene	-	6.0

TABLE XI (continued)

Sample	Appearance		Odour		VCC % w/w
	Before Removal of VCC*	After Removal of VCC	Before Removal of VCC*	After Removal of VCC	
OP-232-50	Cloudy/Amber Red	Clear/Normal	Kerosene	Normal	5.4
OP-232-51	Cloudy/Dark Brown	N.C.	Kerosene	-	7.1
OP-232-52	Cloudy/Dark Brown	N.C.	Kerosene	-	6.9
OP-232-53	Cloudy/Amber Brown	Clear	Kerosene	Normal	10
OP-232-54	Cloudy/Amber Brown	Clear	Kerosene	Normal	11
OP-232-55	Cloudy/Pale Amber	Clear	Kerosene	Normal	6.9
OP-232-56	Cloudy/Pale Amber	Clear	Chlorinated Solvent	Normal	19
OP-232-57	Cloudy/Amber Red	Clear	Kerosene	Normal	16
OP-232-58	Cloudy/Amber Red	N.C.	Kerosene & Chlorinated Solvent	-	20
OP-232-59	Cloudy/Amber Red	Clear	Kerosene	Normal	36

N.C. = No Change

* Brought forward from Table VIII

TABLE XII

Results Obtained Upon Filtration of MQPI Group I Samples
Exhibiting Abnormal Appearance After Removal of VCC

Sample	Appearance		Odour	
	Before Filtration	After Filtration	Before Filtration	After Filtration
EOARD 1	Abnormal	N.C.	-	-
EOARD 5	Abnormal	Normal	-	Normal
OP-232-49	Abnormal	Normal	-	Normal
OP-232-51	Abnormal	Normal	-	Normal
OP-232-52	Abnormal	Normal	-	Normal
OP-232-58	Abnormal	Normal	-	Normal

N.C. = No Change

TABLE XIII

Additional Test Results Obtained on Rejected Samples
EOARD 1 and OP-232-59 After Removal of VCC

	EOARD 1	OP-232-59
KV @		
100°F	19.6	21.4
210°F	4.27	5.10
Sap. mgKOH/g	330	283
MOC % w/w	> 5	> 5
Sp. Gr. 60°F/70°C	0.943	-

TABLE XIV

Volatile Contaminant Contents of MPI Group II Samples
and the Effect of Removing VCC Upon Odour

	Odour		VCC % w/w
	Before Removal of VCC*	After Removal of VCC	
OP-232-4	Slightly Phenolic	Normal	1.7
OP-232-44	Faintly Sweet	Normal	1.3
EDARD 6	Sweet	Normal	6.4

* Brought forward from Table IX

TABLE XV

VHC Screening of MQPI Group III Samples

Sample	VHC % w/w	
	< 1	> 1
OP-232-1	0.1	
OP-232-2	0.2	
OP-232-3	0.1	
OP-232-5	0.2	
OP-232-6	0.2	
OP-232-7	0.2	
OP-232-8	0.2	
OP-232-9	0.1	
OP-232-10	0.2	
OP-232-11	0.2	
OP-232-12	0.2	
OP-232-13	Not Determined (Excessive Water)	
OP-232-14		5
OP-232-15		1.1
OP-232-16	0.4	
OP-232-17	0.3	
OP-232-18	0.8	
OP-232-19	0.3	
OP-232-20		1.3
OP-232-21	0.8	
OP-232-22	0.3	
OP-232-23	0.1	
OP-232-24	0.2	
OP-232-25		> 10
OP-232-26	0.1	

TABLE XV (continued)

Sample	VHC % w/w	
	< 1	>1
OP-232-27	0.2	
OP-232-29	0.1	
OP-232-30	<0.1	
OP-232-31	<0.1	
OP-232-32	0.2	
OP-232-33	0.3	
OP-232-34	0.1	
OP-232-35		>10
OP-232-36		7
OP-232-38		>10
OP-232-39		6
OP-232-40		5
OP-232-41		9
OP-232-42		2
OP-232-43	0.1	
EOARD 2		1.2
EOARD 7		1.2
CONTAINER 1		6.8
CONTAINER 4		2.7
OP-232-47		7.3
OP-232-48		10.5
	28 Samples	17 Samples

4.1.3.2 Samples Containing More Than 1% VCC

These samples were next screened in accordance with Fig. 11 by determining their volatile contaminant contents by means of STM No. 1, the results for which are presented in Table XVI in which are brought forward from Table XV for direct comparison their volatile hydrocarbon contents.

The volatile contaminant contents of the samples are seen to range from 0.8 to 9.0% which are not outside the acceptance limit for VCC in Fig. 11. All seventeen samples were, therefore, released for MQFI in accordance with Fig. 11.

The VHC results in general are seen in Table XVI to exceed those obtained for VCC, this suggesting the hydrocarbon contaminants to be somewhat richer in heavier fractions than those in Avtur and Avgas kerosene-type fuels for example. This could arise from contamination of engine lubricant by turbine fuel under conditions in which lighter fractions of the fuel volatilise from the hot lubricant and escape from the system.

4.2 Volatile Contaminant Distillates from Application of STM No. 1

The used lubricant samples to which STM No. 1 was applied in accordance with the MQPI are listed in Table XVII in which are recorded the appearances and odours of the volatile contaminant distillates obtained. All the distillates were clear mobile fluids smelling of kerosene hydrocarbons and ranging in colour from water-white to strong yellow.

It is pertinent to note that the distillates obtained from samples acquired before 82 February 28 (Table VII) were all water-white in appearance, whereas with the single exception of the distillate from OP-232-56, those obtained from samples received afterwards were coloured. The latter samples may have been taken from accumulations of used lubricant in vessels which had not been allocated for receiving used lubricant exclusively, and may not, therefore, be representative of used lubricant collected under non-ideal conditions in which, however, reasonable care is taken to ensure exclusion of other waste materials from vessels employed for storing the used lubricant. Samples received before 82 February 28 may have been taken directly from engines during oil drain where the hazard of contamination by other materials is more remote.

The volatile contaminants in all the samples are concluded to consist mainly of kerosene hydrocarbons, those submitted after 82 February 28, except OP-232-56, containing also small amounts of other volatile contaminants responsible for the differences in the colours of the distillates obtained.

TABLE XVI

VCC Screening of MQPI Group III Samples
Containing More Than 1% VHC

Sample	VCC % w/w	VHC % w/w*
OP-232-14	4.4	5
OP-232-15	0.9	1.1
OP-232-20	0.8	1.3
OP-232-25	9.0	>10
OP-232-35	7.8	>10
OP-232-36	6.6	7
OP-232-38	6.5	>10
OP-232-39	5.2	6
OP-232-40	5.2	5
OP-232-41	5.6	9
OP-232-42	1.7	2
EOARD 2	0.9	1.2
EOARD 7	0.9	1.2
CONTAINER 1	5.9	6.8
CONTAINER 4	2.3	2.7
OP-232-47	7.4	7.3
OP-232-48	11	10.5

* Brought Forward From Table XV

TABLE XVII

Volatile Contaminant Distillates from
Application of STM No. 1

Sample	Appearance of Distillate	Odour of Distillate
OP-232-4	Clear/Water-White	Kerosene
OP-232-14	Clear/Water-White	Kerosene
OP-232-15	Clear/Water-White	Kerosene
OP-232-20	Clear/Water-White	Kerosene
OP-232-25	Clear/Water-White	Kerosene
OP-232-35	Clear/Water-White	Kerosene
OP-232-36	Clear/Water-White	Kerosene
OP-232-37	Clear Water-White	Kerosene
OP-232-38	Clear/Water-White	Kerosene
OP-232-39	Clear/Water-White	Kerosene
OP-232-40	Clear Water-White	Kerosene
OP-232-41	Clear/Water-White	Kerosene
OP-232-42	Clear/Water-White	Kerosene
OP-232-44	Clear Faintly Straw	Kerosene
OP-232-45	Clear/Faintly Straw	Kerosene
OP-232-46	Clear/Faintly Yellow	Kerosene
EOARD 1	Clear/Faintly Yellow	Kerosene
EOARD 2	Clear/Strongly Yellow	Kerosene
EOARD 3	Clear/Faintly Yellow	Kerosene
EOARD 4	Clear/Faintly Straw	Kerosene
EOARD 5	Clear/Strongly Yellow	Kerosene
EOARD 6	Clear/Faintly Yellow	Kerosene
EOARD 7	Clear/Strongly Yellow	Kerosene
CONTAINER 1	Clear/Faintly Yellow	Kerosene
CONTAINER 2	Clear/Faintly Straw	Kerosene
CONTAINER 3	Clear/Faintly Yellow	Kerosene
CONTAINER 4	Clear/Faintly Yellow	Kerosene
OP-232-47	Clear/Strongly Yellow	Kerosene

TABLE XVII (continued)

Sample	Appearance of Distillate	Odour of Distillate
OP-232-48	Clear/Strongly Yellow	Kerosene
OP-232-49	Clear/Faintly Straw	Kerosene
OP-232-50	Clear/Faintly Straw	Kerosene
OP-232-51	Clear/Faintly Amber	Kerosene
OP-232-52	Clear/Straw	Kerosene
OP-232-53	Clear/Strongly Amber	Kerosene
OP-232-54	Clear/Strongly Amber	Kerosene
OP-232-55	Clear/Faintly Amber	Kerosene
OP-232-56	Clear/Water-White	Kerosene
OP-232-57	Clear/Faintly Yellow	Kerosene
OP-232-58	Clear/Faintly Yellow	Kerosene
OP-232-59	Clear/Faintly Yellow	Kerosene

4.3 Application of MQFI

It has been shown in the foregoing that of the seventy-one samples of used lubricant received, sixty-seven were released by MQFI for carrying out the MQFI. Accordingly, these were examined by the MQFI scheme in Fig. 12 after removal of volatile contaminants and filtration where previously indicated by the MQFI. The results are presented in Table XVIII in which are also presented, although not requirements of the MQFI, results obtained for TAN and KV @ 210°F. The following comments are relevant:-

TAN

TAN was determined by titration in the cold with aqueous standard alkali, and, therefore, represented the extensity of acidity due, not only to carboxylic acids, but also to any amphoteric additives present. In the absence of such additives, the TAN results would be the same as those furnished by ASTM D664 (2) and, as shown by HPLC results presented later, the more common metal passivators BTZ and ABA were not found.

The total acid numbers of twenty-four of the samples are seen to exceed the MIL-L-7808 maximum of 0.30 for unused lubricant, and OP-232-4 stands out by possessing the high TAN of 1.91. This, however, presents no problem in the application of the reclamation technology.

Saponification Value

Based upon the classification given in (3), and taking into consideration the effect of mineral oil, the saponification values indicate that, as a first approximation, the base-stock components of five of the samples to be predominantly diester, those of thirty-eight to be diester/polyol ester mixtures, and those of the remaining twenty-four to be predominantly polyol ester.

Chlorine

The samples were tested for chlorine by fusion of 1 ml. aliquots with sodium (Lassaigne's Test), and identification as silver chloride after expulsion of any hydrocyanic acid from the acidified water extract of the sodium salt. The intensities of the silver chloride opalescence were compared visually with that produced in parallel upon adding silver nitrate solution to an acidified solution of silver chloride equivalent to 0.01% chlorine.

Adjudged in this way, the chlorine contents of all the samples, excepting EOARD 4 and EOARD 5, are seen to be less than 0.01%, this indicating absence of chlorine-containing additives. This was checked quantitatively in the case of OP-232-2 and OP-232-41, selected at random, by determining their chlorine contents in accordance with IP.118/65 (joint ASTM 317-64) except that due to malfunctioning of the potentiometric equipment which was under repair, the chlorine ions were precipitated and determined

TABLE XVIII

MQFI Results Obtained for Samples Complying with MQPI Requirements

Sample	KV @		MOC %	Sap. Value	Foam		Cl %	TAN*
	100°F	210°F*			Vol. ml.	Collapse secs.		
OP-232-1	14.9	3.48	<5	331	130	30	<.01	0.67
OP-232-2	14.2	3.37	<5	342	30	7	<.01	0.10
OP-232-3	14.5	3.41	<5	346	10	5	<.01	0.07
OP-232-4	15.0	3.54	<5	312	>500	88	<.01	1.91
OP-232-5	15.4	3.56	<5	331	30	8	<.01	0.18
OP-232-6	13.7	3.38	<5	305	30	8	<.01	0.67
OP-232-7	13.8	3.39	<5	304	30	9	<.01	0.93
OP-232-8	13.7	3.42	<5	306	30	8	<.01	0.76
OP-232-9	13.7	3.43	<5	311	40	9	<.01	0.73
OP-232-10	13.8	3.43	<5	309	50	12	<.01	1.01
OP-232-11	13.7	3.36	<5	307	80	15	<.01	0.75
OP-232-12	13.7	3.37	<5	307	80	8	<.01	0.79
OP-232-14	14.4	3.44	<5	314	210	30	<.01	0.12
OP-232-15	14.3	3.42	<5	325	400	40	<.01	0.12
OP-232-16	14.1	3.41	<5	317	100	15	<.01	0.13
OP-232-17	14.1	3.39	<5	310	10	4	<.01	0.25
OP-232-18	14.2	3.44	<5	313	80	15	<.01	0.17
OP-232-19	14.2	3.42	<5	320	10	15	<.01	0.12
OP-232-20	14.1	3.40	<5	319	430	58	<.01	0.13

TABLE XVIII (continued)

Sample	KV @		MDC %	Sap. Value	Foam			CI %	TAN*
	100°F	210°F*			Vol. ml.	Collapse secs.			
OP-232-21	14.2	3.41	<5	322	100	20	<.01	<.01	0.10
OP-232-22	14.7	3.45	<5	327	10	4	<.01	<.01	0.15
OP-232-23	14.7	3.45	<5	331	10	4	<.01	<.01	0.13
OP-232-24	14.0	3.38	<5	310	30	8	<.01	<.01	0.49
OP-232-25	13.9	3.36	<5	308	140	30	<.01	<.01	0.13
OP-232-26	15.4	3.66	<5	300	50	12	<.01	<.01	1.68
OP-232-27	14.8	3.50	<5	324	20	5	<.01	<.01	0.27
OP-232-28	14.1	3.40	<5	311	30	15	<.01	<.01	0.18
OP-232-29	15.2	3.58	<5	308	10	4	<.01	<.01	1.12
OP-232-30	14.4	3.93	<5	328	30	8	<.01	<.01	0.12
OP-232-31	14.9	3.19	<5	333	40	15	<.01	<.01	0.16
OP-232-32	14.2	3.41	<5	311	40	20	<.01	<.01	0.16
OP-232-33	13.6	3.54	<5	279	30	8	<.01	<.01	0.43
OP-232-34	13.4	3.40	<5	286	30	10	<.01	<.01	1.46
OP-232-35	14.3	3.37	<5	325	45	35	<.01	<.01	0.11
OP-232-36	14.7	3.44	<5	343	210	25	<.01	<.01	0.15
OP-232-37	13.1	3.41	<5	298	240	46	<.01	<.01	0.15
OP-232-38	14.3	3.40	<5	326	240	40	<.01	<.01	0.20

TABLE XVIII (continued)

Sample	KV @		MOC %	Sap. Value	Foam		Cl %	TAN*
	100°F	210°F*			Vol. ml.	Collapse secs.		
OP-232-39	14.3	3.37	<5	340	110	25	<.01	0.11
OP-232-40	14.6	3.40	<5	316	210	55	<.01	0.17
OP-232-41	14.3	3.39	<5	312	30	15	<.01	0.12
OP-232-42	14.3	3.44	<5	307	290	35	<.01	0.27
OP-232-43	14.7	3.48	<5	307	40	10	<.01	1.12
OP-232-44	14.3	3.44	<5	301	260	40	<.01	0.36
OP-232-45	14.2	3.46	<5	298	50	15	<.01	0.19
OP-232-46	14.2	3.45	<5	309	70	15	<.01	0.16
EOARD 2	13.7	3.37	<5	286	500	48	<.01	0.35
EOARD 3	13.9	3.39	5	301	>500	59	<.01	0.57
EOARD 4	15.4	3.65	>5	295	>500	45	0.10	0.73
EOARD 5	14.2	3.47	5	287	>500	60	0.10	0.31
EOARD 6	14.3	3.42	<5	323	>500	45	<.01	0.24
EOARD 7	14.5	3.43	<5	304	500	60	<.01	0.52
CONTAINER 1	13.7	3.34	<5	316	180	12	<.01	0.22
CONTAINER 2	13.7	3.35	<5	306	500	45	<.01	0.21
CONTAINER 3	13.6	3.33	<5	306	500	45	<.01	0.21
CONTAINER 4	13.8	3.31	<5	289	440	39	<.01	0.13

TABLE XVIII (continued)

Sample	KV @		MOC %	Sap. Value	Foam		Cl %	TAN*
	100°F	210°F*			Vol. ml.	Collapse secs.		
OP-232-47	25.0	4.99	<5	336	350	50	<.01	0.15
OP-232-48	26.8	5.42	<5	333	400	73	<.01	0.10
OP-232-49	14.2	3.40	<5	306	>500	36	<.01	0.31
OP-232-50	14.2	3.42	>5	282	>500	45	<.01	0.25
OP-232-51	22.3	4.55	>5	340	450	80	<.01	0.35
OP-232-52	21.5	4.47	5	333	475	99	<.01	0.35
OP-232-53	23.5	4.74	>5	324	>500	60	<.01	0.18
OP-232-54	20.3	4.28	>5	348	200	25	<.01	0.21
OP-232-55	14.7	3.52	<5	309	200	25	<.01	0.26
OP-232-56	14.8	3.54	<5	309	150	20	<.01	0.21
OP-232-57	17.1	4.10	>5	297	500	63	<.01	0.31
OP-232-58	16.7	4.02	>5	290	500	78	<.01	0.33

* Not Required by MQFI

gravimetrically as silver chloride. The results obtained were:-

OP-232-2	0.007% chlorine
OP-232-41	0.005% chlorine

With regard to EOARD 4 and EOARD 5, these are seen to exhibit relatively high chlorine contents of the order of 0.1% which was not, however, investigated further because, as shown below, EOARD 4 failed to comply with the MQFI requirements, and EOARD 5 was placed by the MQFI among the thirty members of Category 3, the dilution effect of which would reduce the chlorine content of the blended components below 0.01%.

Foaming Propensity

Foaming propensity was determined in accordance with Fed. Std. Method 3212.

Thirty-two samples are seen to exhibit foam volumes and collapse times below the MIL-L-7808 maximum limits of 100 ml. and 60 secs. respectively.

The remaining thirty-five samples, however, are seen to exhibit foam volumes greater than 100 ml., six of these exhibiting collapse times greater than 60 secs. It is pertinent to note that seventeen samples produced foam volumes greater than 430 ml., and that these exceptionally high foamers, which are seen to include the six samples exhibiting high foam-collapse times, are among samples received after 82 February 28 (Table VII) as was the case with samples producing coloured volatile contaminant distillates (page 53).

KV @ 100°F and MOC

It is seen that ten samples fail to comply with the MQFI requirements, three failing on account of high KV, four on account of excessive MOC, and three on account of both high KV and excessive MOC. The following comments and conclusions are relevant to these samples.

EOARD 4, OP-232-50, OP-232-57 and OP-232-58 are concluded to comprise MIL-L-7808 arisings excessively contaminated by mineral oil.

OP-232-47 and OP-232-48 possess viscosities and saponification values more typical of 5 cSt. polyol ester lubricant than the 3 cSt. polyol ester type, and their specific gravities, which @ 70°F were found to be 0.982 and 0.978 respectively, are typical of the 5 cSt. type lubricant. Furthermore, chromatograms obtained from GLC analysis of the samples were seen to exhibit a greater proportion of high boiling base-stock components than one which was obtained from OP-232-41 complying with the MQFI requirements, and they closely resembled in this respect the chromatogram obtained for a commercial 5 cSt. polyol ester turbine engine lubricant*. It is concluded

* Esso Turbo Oil 25

from these results that the two samples had been taken from arisings of MIL-L-23699 rather than MIL-L-7808 type lubricant.

OP-232-52 also is seen to fail against the MQFI on account of high viscosity which, however, is somewhat low for a 5 cSt. polyol ester lubricant. Taking into account the presence of 5% mineral oil, and the possible presence of volatile hydrocarbon contaminants not removed by SLM No. 1 (page 14), and which may be expected to lower viscosity somewhat, the conclusion is drawn that this sample, too, had been taken from MIL-L-23699 arisings, a conclusion which is supported by the high saponification value, and also by the specific gravity of the sample, which @ 70°F was found to be 0.969.

OP-232-51, OP-232-53 and OP-232-54 are concluded, from their high viscosities and high saponification values, and their high mineral oil contents, to consist of MIL-L-23699 arisings excessively contaminated by mineral oil.

Again, it is pertinent to note that all the ten samples rejected by the MQFI were received after 82 February 28, i.e., among the last twenty-seven of the total of seventy-one samples of used lubricant received.

4.3.1 Category Characterisation

The categories into which the sixty-seven samples fall are illustrated in Tables XIX, XX and XXI where they are seen to fall into the following three of the five categories of the MQFI scheme in Fig. 12.

Category 1 (Reject)	- 10 samples
Category 3 (High foam, low chlorine)	- 30 samples
Category 5 (Low foam, low chlorine)	- 27 samples

Expressed on total number of used lubricant samples received viz., seventy-one, 15.5% of the samples fall into Category 1, 42.3% fall into Category 3, 38.0% fall into the least contentious Category 5, and the remaining 4.2% comprise the four samples which failed against the MQFI (page 44 and 45). Thus, at least 19.7% of the samples are unacceptable for reclamation on account of inadequate house-keeping in their collection.

4.4 HPLC Analysis and Quinizarin

By way of providing additional data of interest, though not required by the MQFI, the unrejected samples after removal of VCC were examined quantitatively by High Performance Liquid Chromatography (HPLC) and qualitatively for the presence of quinizarin (QZ).

The HPLC analyses were performed in accordance with the

TABLE XIX

MQFI Classification of Samples

Category 1 - Reject

Sample	Reason for Rejection	Conclusion
EOARD 4	High MOC	MIL-L-7808 arisings excessively contaminated by mineral oil
OP-232-47 OP-232-48 OP-232-52	High KV	MIL-L-23699 arisings
OP-232-50	High MOC	MIL-L-7808 arisings excessively contaminated by mineral oil
OP-232-51	High KV and MOC	MIL-L-23699 arisings excessively contaminated by mineral oil
OP-232-53		
OP-232-54		
OP-232-57 OP-232-58	High MOC	MIL-L-7808 arisings excessively contaminated by mineral oil

10 Samples

TABLE XX

MQFI Classification of Samples
Category 3 - High Foam, Low Chlorine

OP-232-1
OP-232-4
OP-232-11
OP-232-12
OP-232-14
OP-232-15
OP-232-16
OP-232-18
OP-232-20
OP-232-21
OP-232-25
OP-232-36
OP-232-37
OP-232-38
OP-232-39
OP-232-40
OP-232-42
OP-232-44
EOARD 2
EOARD 3
EOARD 5
EOARD 6
EOARD 7
CONTAINER 1
CONTAINER 2
CONTAINER 3
CONTAINER 4
OP-232-49
OP-232-55
OP-232-56

Foam Volumes Mean = >293 ml.
Range = 80 to >500

Number of samples producing foam
volumes of less than 100 ml. = 3

30 Samples

TABLE XXI

MQFI Classification of Samples
Category 5 - Low Foam, Low Chlorine

OP-232-2
OP-232-3
OP-232-5
OP-232-6
OP-232-7
OP-232-8
OP-232-9
OP-232-10
OP-232-17
OP-232-19
OP-232-22
OP-232-23
OP-232-24
OP-232-26
OP-232-27
OP-232-28
OP-232-29
OP-232-30
OP-232-31
OP-232-32
OP-232-33
OP-232-34
OP-232-35
OP-232-41
OP-232-43
OP-232-45
OP-232-46

Foam Volumes Mean = 30 ml.
Range = 10 to 70 ml.

27 Samples

methodology given in Appendix F which was devised to produce with each sample in 15 to 20 minutes a chromatograph giving good resolution of peaks produced by the inhibitors DODP, PAN, MOPAN, DOPT, NADOPT, NBDOP, PTZ and one or the other of those produced by BTZ and ABA; the last two inhibitors are not differentiated from one another under the conditions employed as their retention times are the same.

The presence of quinizarin was tested by shaking an aliquot of each sample with powdered calcium hydroxide which, in the presence of concentrations of QZ exceeding 0.1 ppm, assumes a purple blue colour, the intensity of which increases with QZ concentrations.

The HPLC results for MQFI Categories 3 and 5 samples are presented in Tables XXII and XXIII respectively in which are also presented the results obtained for QZ.

Referring to the HPLC results, it is seen that apart from the low PAN content of EOARD 6, DODP and PAN are the only inhibitors found in all the samples which are present in significant concentrations, these two inhibitors together being recognised as an effective antioxidant system. The low PAN content of EOARD 6 (Table XXII) and the relatively low concentrations of PAN found in OP-232-26/29/33/34 and 43 (Table XXIII) may be explained on the supposition that the PAN contents of the original lubricants had suffered partial oxidation in service with the formation of products still functioning as an antioxidant and/or synergist, but which did not appear in the chromatogram.

It is seen that MOPAN was found in thirty-five of the samples in concentrations which, however, with the possible exception of OP-232-18 (Table XII), are considered to be too low to be of any functional significance.

The absence of BTZ and ABA in all the samples is rather surprising, but it is possible that either may have been present in the original lubricants, and had become depleted in service as a result of "plating out" in fulfilling its protective role of metal passivator/deactivator.

Referring to the results obtained for QZ, it is seen that this inhibitor was found in ten of the fifty-seven samples, only six of which were found to contain QZ in significant concentration, i.e., > 100 ppm.

5. Reclamation Feedstocks

Three feedstocks were prepared by blending together samples of like MQFI category with the original intention of submitting each blend to the reclamation exercise. New barrels of 45 UK gallon capacity were scrupulously cleaned for this purpose and labelled with the correct category numbers. Samples in each category were

TABLE XXII

HPLC Results and Quinizarin - MQFI Category 3 Samples After Removal of VCC

Sample	DODP %	PAN %	MQPAN %	DOPT %	NADOPT %	NBDOPT %	PTZ %	(BTZ + ABA) %	QZ
OP-232-1	1.2	0.5	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-4	1.2	0.4	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-11	1.4	0.6	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-12	1.5	0.6	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-14	1.5	0.6	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-15	1.4	0.7	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-16	1.4	0.7	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-18	1.4	0.6	.23	<.01	<.01	<.01	<.005	<.005	nf
OP-232-20	1.4	0.6	.03	<.01	<.01	<.01	<.005	<.005	nf
OP-232-21	1.4	0.7	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-25	1.5	0.6	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-36	1.4	0.7	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-37	1.4	0.6	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-38	1.4	0.6	.04	<.01	<.01	<.01	<.005	<.005	nf

TABLE XXII (continued)

Sample	DODP %	PAN %	MDPAN %	DOPT %	NADOPT %	NBDOPT %	PTZ %	(BTZ + ABA) %	QZ
OP-232-39	1.5	0.8	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-40	1.4	0.7	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-42	1.5	0.6	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-44	1.5	0.5	<.006	<.01	<.01	<.01	<.005	<.005	nf
EOARD 2	1.5	0.4	.05	<.01	<.01	<.01	<.005	<.005	>100 ppm
EOARD 3	1.3	0.4	.17	<.01	<.01	<.01	<.005	<.005	>100 ppm
EOARD 5	1.2	0.4	.06	<.01	<.01	<.01	<.005	<.005	>100 ppm
EOARD 6	1.4	0.07	.01	<.01	<.01	<.01	<.005	<.005	nf
EOARD 7	1.3	0.6	<.006	<.01	<.01	<.01	<.005	<.005	>100 ppm
CONTAINER 1	1.4	0.7	.01	<.01	<.01	<.01	<.005	<.005	<0.1 ppm
CONTAINER 2	1.5	0.6	.01	<.01	<.01	<.01	<.005	<.005	<0.1 ppm
CONTAINER 3	1.5	0.7	.02	<.01	<.01	<.01	<.005	<.005	<0.1 ppm
CONTAINER 4	1.4	0.7	<.006	<.01	<.01	<.01	<.005	<.005	<0.1 ppm
OP-232-49	1.4	0.7	.01	<.01	<.01	<.01	<.005	<.005	nf

TABLE XXII (continued)

Sample	DODP %	PAN %	MOPAN %	DOPT %	NADOPT %	NBDOPT %	PTZ %	(BTZ + ABA) %	QZ
OP-232-55	1.2	0.7	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-56	1.2	0.7	.02	<.01	<.01	<.01	<.005	<.005	nf

nf = not found

TABLE XXIII

HPLC Results and Quinizarin - MQFI Category 5 Samples After Removal of

Sample	DODP %	PAN %	MDPAN %	DOPT %	NADOPT %	NBDOPT %	PIZ %	BIZ + ABA %	42
OP-232-2	1.4	0.8	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-3	1.4	1.0	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-5	1.4	0.6	nf	<.01	<.01	<.01	<.005	<.005	>100 ppm
OP-232-6	1.5	0.6	.03	<.01	<.01	<.01	<.005	<.005	nf
OP-232-7	1.5	0.6	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-8	1.5	0.6	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-9	1.5	0.6	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-10	1.5	0.6	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-17	1.3	0.5	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-19	1.4	0.7	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-22	1.4	0.6	.03	<.01	<.01	<.01	<.005	<.005	nf
OP-232-23	1.5	0.7	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-24	1.4	0.5	.01	<.01	<.01	<.01	<.005	<.005	nf
OP-232-26	1.1	0.3	.14	<.01	<.01	<.01	<.005	<.005	nf

TABLE XXIII (continued)

Sample	DNDP %	PAN %	MOPAN %	DODPT %	NADOPT %	NBDOPT %	PTZ %	(BTZ + ABA) %	QZ
OP-232-27	1.5	0.6	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-28	1.0	0.5	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-29	1.2	0.3	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-30	1.5	0.7	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-31	1.5	0.7	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-32	1.4	0.7	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-33	2.3	0.3	nf	<.01	<.01	<.01	<.005	<.005	>100 ppm
OP-232-34	1.9	0.1	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-35	1.4	0.8	<.006	<.01	<.01	<.01	<.005	<.005	nf
OP-232-41	1.4	0.7	.02	<.01	<.01	<.01	<.005	<.005	nf
OP-232-43	1.2	0.3	nf	<.01	<.01	<.01	<.005	<.005	nf
OP-232-45	1.3	0.5	.04	<.01	<.01	<.01	<.005	<.005	nf
OP-232-46	1.4	0.5	.06	<.01	<.01	<.01	<.005	<.005	nf

nf = not found

introduced into the appropriate barrel which was then rolled and up-ended several times to ensure adequate mixing of the contents.

Two barrels were necessary for holding each of Category 3 and 5 samples, the contents of which were transferred to a pilot plant holding tank and mixed by agitation before returning them to the barrels. The holding tanks had been cleaned thoroughly and flushed with arisings of a MIL-L-7808 type lubricant from Rolls-Royce which was then allowed to drain from the tank. It was known that residual drag-out oil, expressed on the volume of the USAF arisings, would amount to not more than 0.05% v/v. This seemed reasonable having regard to the desirability of conserving as much of the USAF arisings as possible at this stage since it was anticipated that at least half would be required for cleaning out the reclamation plant.

Only two of the three feedstocks, viz., those comprising Categories 3 and 5 samples, were in fact submitted to the reclamation exercise for reasons which are apparent in the following comments.

5.1 MQFI Category 3 Feedstock (High Foam, Low Chlorine)

The crucial question here is whether the reclamation technology is effective in lowering the foaming propensity below the maximum allowable in MIL-L-7808, otherwise there is no reason why this feedstock should not be reclaimable. Experience has shown the technology to be effective, with few exceptions, in lowering the foaming propensities of commercial arisings of diester and polyol ester lubricants but, due to the complexity of factors involved in foaming, it is impossible to generalise on this subject.

5.2 MQFI Category 5 Feedstock (Low Foam, Low Chlorine)

This is the least contentious feedstock, and from the results of earlier research (1) should be reclaimable.

5.3 MQFI Category 1 Feedstock (Reject)

This feedstock is not, in accordance with the MQFI scheme, acceptable for reclamation. However, it was intended within the scope of the present research to demonstrate the non-reclaimability of such material by submitting it to the reclamation technology unless it was unequivocally evident from the inspection results to be non-reclaimable.

Referring to Table XIX, six of the ten rejected samples were concluded to have been taken from MIL-L-23699 arisings on the evidence of viscosity and other test data (pages 63 and 64), their high viscosities alone definitely ruling out any hope of reclaiming them to the requirements of MIL-L-7808.

The remaining four rejected samples were concluded to have been taken from MIL-L-7808 arisings contaminated, however, by more than 5% w/w mineral oil. They were rejected on the grounds that mineral oils falling outside the definition of volatile hydrocarbon contaminants (page 14) are not removed by the reclamation technology, and that in the experience of Dalton concentrations exceeding 5% are sufficient in general to jeopardise compliance of the reclaimed product with requirements for low-temperature fluidity. Some justification, therefore, existed for demonstrating the non-reclaimability of these arisings by way of checking the validity of the Dalton experience in so far as MIL-L-7808 arisings are concerned.

The samples, however, totalled only 67 kg which was too small for processing in the reclamation plant. Consideration was given to the feasibility of demonstrating non-reclaimability of the material in a Laboratory simulation of the reclamation plant, but this was concluded to be unrealistic since the equipment intended for this purpose failed to reproduce all the conditions prevailing in the large-scale plant, and any results obtained would have been, therefore, questionable.

The most likely mineral oil contaminant which might be acceptable in concentrations exceeding 5% in MIL-L-7808 arisings was envisaged to be hydraulic fluid MIL-H-5606B in view of its low viscosity. It was pertinent, therefore, to enquire whether this fluid falls within, or outside, the definition of VCC (page 5) since in the former case none would appear as MOC in the application of the MQFI for the latter is carried out after removal of VCC by means of STM No. 1.

The most direct way of determining this would have been to contaminate a sample of unused MIL-L-7808 lubricant with a known amount of the fluid, and then to determine VCC by means of STM No. 1 followed perhaps by determination of the flash-point of the residue. However, due to time constraints, this could not be accomplished, but some preliminary information was obtained by applying STM No. 2 to a sample of the hydraulic fluid. 85% of the fluid was seen to appear in the chromatogram as VHC ahead of the hexadecane marker (bp 287°C), and 36% was seen to appear as VCC ahead of the n-tridecane marker (bp 235.5°C).

Deduced from these results, the concentration of MIL-H-5606B which would appear as 5% MOC in the MQFI is of the order of $5 \times 100 / (100 - 36) = 8\%$, the components thereof comprising higher boiling fractions which would be expected to exhibit not only higher flash-point, but to be more viscous, and, therefore, more prone to impair low temperature fluidity than the hydraulic fluid itself.

6. Reclamation

The two feedstocks were processed in the same plant, and under the same operational conditions as those employed in the previous research contract (1).

446 and 422 kg of Categories 3 and 5 feedstocks were available, but about half of each was employed for cleaning out the plant which in each case had been previously engaged in processing production batches of MIL-L-23699 arisings from Rolls-Royce. These preliminary cleaning operations were considered to be particularly important in view of the tight restriction on foaming propensity by MIL-L-7808, and the sensitivity of the foaming test to traces of foreign materials.

6.1 Processed Feedstocks

The processed material, i.e., the reclaimed product prior to additive treatment, amounted in each case to 80% of feedstock.

The results of partial examination of the processed feedstocks at this stage are presented in Table XXIV in which the highlight is seen to be the substantial reduction in foaming propensity of the high-foam Category 3 feedstock, the results obtained for both the processed feedstocks falling well below the MIL-L-7808 maximum limits of 100 ml. foam and 60 secs. collapse time.

Comparing the concentrations of inhibitors found in the two processed feedstocks with those found in the individual components thereof prior to processing (Tables XXII and XXIII), the conclusion is drawn that no loss in these inhibitors had occurred during the processing.

The total acid numbers obtained for both Categories are seen to be somewhat high, the TAN of Category 5 just complying with the MIL-L-7808 requirement of 0.30 max., and that of Category 3 exceeding this limit, but falling below the MIL-L-23699 limit of 0.50 max. Total acid numbers of the order of 0.10 should have been realised, the high numbers obtained having been due to malfunctioning of equipment in the reclamation plant for reducing acidity, the cause of which is understood. Unfortunately, due to time constraints, it was not possible to dismantle the equipment and rectify the trouble before carrying out the processing. Thus, although the TAN of Category 3 exceeds the MIL-L-7808 limit, it is not indicative of non-reclaimability under normal plant operation, and it can be categorically stated from experience in the reclamation of Rolls-Royce turbine engine lubricant arisings, that the TAN of 0.41 would have no adverse effect during an engine evaluation of the material.

6.2 Additive Treatment

No information was available on the additive contents of the lubricants from which the components of the two feedstocks had arisen, and it was decided, on the basis of experience, to introduce BTZ and tritolyl phosphate (TTP) into the two processed feedstocks, and to increase the concentrations of PAN.

TABLE XXIV

Test Results on Processed Feedstocks Prior to Additive Treatment

		Category 3	Category 5
Transparency		Sparkling Clear	Sparkling Clear
Colour		Pale Amber	Pale Amber
Flash Point °F (Note 1)		460	450
KV @	210°F	3.38	3.34
	100°F	13.9	13.6
TAN - mgKOH/g (Note 2)		0.41	0.30
Phosphorus (expressed as P%)		0.10	0.09
Foam Test (Method 3213)	Foam Vol. - ml.	40	25
	Collapse - secs.	9	5
DODP %		1.46	1.51
PAN %		0.62	0.59
MOPAN %		0.017	0.018
BTZ %		nf	nf
QZ %		<.007	<.004

nf = not found

Note 1: ASTM D.92Note 2: Titrated cold with aqueous standard alkali

It was anticipated, also from experience, that with the exception of BTZ, these additives would increase the foaming propensities of the feedstocks, and the extent to which the concentrations could be increased would be, therefore, limited by the tight restriction on foaming imposed by MIL-L-7808. This was indeed observed as illustrated in Tables XXV and XXVI in which are presented the results of foaming tests carried out on aliquots of the two processed feedstocks after increasing their additive contents by the amounts shown. The last but one column of each of these Tables shows the increases which were finally decided for treating the feedstocks, and the last columns show the expected additive contents of the treated feedstocks as calculated from these increases and the determined additive contents of the processed feedstocks (Table XXIV). The sources of the additives employed are given in Table XXVII, and total TTP contents were calculated on the assumption that the determined phosphorus contents of the processed feedstocks existed in the form of Reolube TTP (phosphorus content = 8.3% w/w).

The additives were incorporated as concentrates prepared by dissolving in a portion of each feedstock fifty-fold the concentrations of additives shown in the last but one columns of Tables XXV and XXVI. Thorough mixing of the concentrates with the feedstocks was accomplished by nitrogen agitation for one hour.

7. Evaluation of Reclaimed Feedstocks

Results obtained upon partial evaluation of the reclaimed feedstocks are presented in Table XXVIII. Within the limited scope of this partial evaluation, both the reclaimed products appeared to be satisfactory, and 294 and 239 kg of Categories 3 and 5 respectively were submitted to AFWAL for complete evaluation.

Referring to Tables XXIV and XXVIII, it is seen that the additive treatment of both feedstocks was accompanied by increases in total acid numbers of about 0.40. This is due to the amphoteric nature of the BTZ additive (2) which is titratable by the aqueous alkali employed in determining the total acid numbers, but which is not titratable by alcoholic potash in non-aqueous media as employed in the determination of TAN by means of ASTM D664 in accordance with MIL-L-7808.

Foaming Propensity vs Additive Additions to Category 3

* Method 3213

TABLE XXVI

Foaming Propensity vs Additive Additions to Category 5

	Increase in Percentage Additives from Additions to Category 5 Distillate					Total Percentage Additives Calculated from Final Decision
	F	G	H	I	Final Decision	
DODP	Nil	Nil	Nil	Nil	Nil	1.51
PAN	Nil	0.23	0.41	0.42	0.42	1.01
MOPAN	Nil	Nil	Nil	Nil	Nil	0.02
BTZ	Nil	0.09	0.09	0.09	0.09	0.09
TTP	Nil	0.42	0.67	0.42	0.42	1.50 (± 0.125 as P)
QZ	Nil	Nil	Nil	Nil	Nil	< .009
Foaming Propensity*	Foam-ml.	25	50	95	70	
	Collapse-secs.	5	25	32	25	

* Method 3213

AD-A158 624

CHARACTERIZATION OF USED MIL-L-7808 LUBRICANTS(U)
DALTON AND CO (SYNTHETIC PRODUCTS) LTD BELPER (ENGLAND)
R A MICALLEF ET AL. MAY 85 AFWAL-TR-85-2017
F49620-81-C-0064

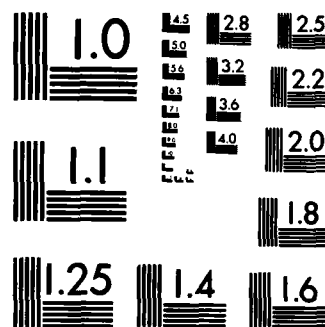
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TABLE XXVII

Additive	Source and Commercial Description of Additive
PAN	Bayer Chemical (1-phenyl-1-naphthylamine)
BTZ	Ciba-Geigy (Purified Benzotriazole)
TTP	Ciba-Geigy (Iritolyl phosphate manufactured from 100% m-cresol. Phosphorous Content = 8.3%)

TABLE XXVIII

Test Result on Reclaimed Feedstocks

			Category 3	Category 5
Transparency			Clear	Clear
Colour			Amber	Amber
Flash Point (ASTM D92) °F			445	450
K.V. @	210°F		3.37	3.33
	100°F		14.0	13.8
TAN (Note 1)			0.80	0.70
Saponification Value			310	306
Phosphorus - as P% (Note 2)			0.13	0.13
Chlorine %			≤0.01	≤0.01
Hydrolytic Liability (RR.1006, Iss.2)	D ⁹⁰ _{1.5} - hrs		59	57
	D ⁷⁰ _{1.5} - hrs		410	390
	D ⁴⁰ _{1.5}	hrs	7,600	7,000
		Lunar Months	3.5	3.1
Foaming Property (Method 3213)	Max. Foam -ml		80	100
	Foam Collapse, secs		25	50
Trace Elements ppm (Note 3)	Aluminium		2	2
	Iron		1	2
	Chromium		≤1	≤1
	Silver		≤1	≤1
	Copper		≤1	≤1
	Tin		7	4
	Magnesium		2	2
	Nickel		≤1	≤1
	Titanium		≤1	≤1
	Dirt Silicon		3	2

Note 1 Sample titrated cold with aqueous standard alkali

Note 2 Determined in accordance with ASTM D1091

Note 3 Spark Emission

Table XXVIII continued

		Category 3	Category 5
Inhibitors %	DODP	1.49	1.53
	PAN	0.80	0.98
	MOPAN	0.02	0.02
	BTZ	0.087	0.084
	QZ	< 0.007	< 0.007

Effective Life in hours @ 180°C

Degradation Mode	Volatilisation Loss	68	73
	Acidity Increase	> 1000	920
	Viscosity Increase	540	330
	Benzene Insolubles Increase	> 1000	> 1000

Effective Life in hours @ 225°C

Degradation Mode	Volatilisation Loss	18	19
	Acidity Increase	8	11
	Viscosity Increase	13	19
	Benzene Insolubles Increase	67	95

Table XXVIII Continued

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C
Confined Heating (R.R. 1004/Supp. 1)

Test Specimen	Metal Weight Change		Appearance of Specimen	
	Category 3	Category 5	Category 3	Category 5
Magnesium Alloy	-5.7	-4.8	$E_g(m)$ $D_g(m)$	$E_g(m)$ $D_g(m)$
Aluminium Alloy	< 0.1	< 0.1	0	0
Mild Steel	< 0.1	< 0.1	0	0
Soldered Copper	< 0.1	< 0.1	$D_g(s)$	$D_g(s)$
Lead	-46	-46	$E_g(m)$	$E_g(m)$
Copper	0.05	0.05	$D_g(s)$	$D_g(s)$
Brass	0.1	0.1	$D_g(s)$	$D_g(s)$

Descriptive Key: 0 = No Change

D = Discoloured

E = Etched
P = Pittedl = Local
g = General(s) = slight
(m) = moderate(x) = excessive
* = deposition of
copper

CONCLUSIONS/RECOMMENDATIONS

1. 19.7% of the used lubricant samples submitted were unacceptable for reclamation on account of inadequate housekeeping in their collection.
2. 71.4% of the unacceptable samples were not distributed about the median of the total samples submitted, but were received after 82 Feb. 28 among the last twenty-seven of the total of seventy-one samples received over the period 81 April - 82 Oct. 31. This indicates significant differences in the modus operandi and/or care taken in the collection of used lubricant at a minor number of Bases, and which might be rectified in future by closer attention to such Bases.
3. 80.3% of total samples submitted conformed to the requirements of the minimum quality specification as potentially reclaimable.
4. 47.4% of the potentially reclaimable samples exhibited low foaming propensities, and when blended together comprised a least contentious feedstock designated Category 5.
5. 52.6% of the potentially reclaimable samples exhibited extremely high foaming propensities, and when blended together comprised a more contentious feedstock designated Category 3.
6. The feedstocks, after processing in the Dalton reclamation plant, exhibited lower foaming propensities, that of Category 3 falling comfortably within the foam requirements of MIL-L-7808.
7. No losses in the additive contents of the feedstocks occurred during the processing.
8. Choice in the maximum concentration of PAN and TTP which were introduced during additive treatment of each processed feedstock was limited jointly by the foaming propensity of the feedstock and the tight restriction on foaming imposed by MIL-L-7808.

9. BTZ, which was also employed in the additive treatment, has no influence on foaming propensity.
10. The oxidation/corrosion characteristics of the two reclaimed products, are tentatively concluded, from the results of partial laboratory evaluation, to be satisfactory in spite of the foam restrictions on the extent of additive treatment which was possible.
11. The yield of reclaimed product is not less than 80% of used lubricant feedstock.
12. Subject to satisfactory results from AFWAL evaluation of the two reclaimed products, it is concluded that the proportion of reclaimable lubricant from USAF arisings of used MIL-L-7808 lubricants is of the order of 80%.
13. The restriction on foaming propensity, as imposed by MIL-L-7808, is concluded to be the most likely factor which in practice will influence the proportion of used lubricant arisings which can be reclaimed to the specification requirements by means of the Dalton technology.
14. Some high-foam arisings could be utilised in practice by blending them with low-foam arisings but, the proportion of reclaimable arisings which might be increased in this way will depend upon the proportion of low-foam arisings available.
15. It is well known that the foaming propensities of synthetic turbine engine lubricants can be lowered by means of commercial silicone antifoam agents but, although this artifice in the case of virgin lubricant is not prohibited by MIL-L-7808, it is not favoured by Dalton since the effect may not be long lasting for reasons which are well understood by AFWAL. It is recommended that the specification prohibit the use of silicone antifoam agents in future submissions of virgin lubricant apart from the use of, if possible, a silicone product especially tailored to ensure long functional life.

REFERENCES

- (1) Reclamation of Synthetic Turbine Engine Lubricants,
Technical Report AFWAL-TR-81-2072.
- (2) Reference (1), page 57.
- (3) Reference (1), Table VIII, page 19.

APPENDIX A

Supplement Test Method No. 1

Determination and Elimination of Volatile Contaminant Content of Used Synthetic Turbine Engine Lubricant

1. Introduction

The method is intended for determining and eliminating the volatile contaminant contents of samples of used diester and polyol ester turbine engine lubricants in preparing such samples for laboratory assessment.

Volatile contaminants are defined herein as those materials in used ester type turbine engine lubricants which are wholly or partially eliminated upon application of Process 1 of the Dalton reclamation technology, an outline of which has been given elsewhere.*

Materials boiling below 235°C @ 760 Torr pressure absolute are almost completely eliminated, whereas the proportion eliminated of those boiling above this temperature decreases rapidly with increasing boiling point. By way of an example, the proportion eliminated of Avtur kerosene type turbine fuel (DERD 2494) contaminant boiling over the range 160°C to 240°C is of the order of 97%.

2. Summary of Method

Approximately 450 ml. of the test sample are heated in a distillation apparatus to 195°C under an absolute pressure of 8 to 12 Torr over a period of approximately 23 minutes, during which a current of nitrogen is passed through the sample. A temperature between 185°C and 195°C is maintained until condensed vapour leaving the stillhead outlet falls below a specified rate, and then, with the nitrogen still flowing, the apparatus is allowed to cool, the residual sample providing, in most cases, sufficient of the "stripped" material for laboratory assessment.

The volatile contaminant content is determined from the loss in weight of the sample. Material collected in the receiver of the distillation apparatus consists of the volatile contaminant of the sample less those volatile contaminants which escape condensation under the test conditions employed.

* USAF Contract No. F.49620-79C-0073, Final Report, Fig. 1

3. Apparatus and Materials

The apparatus consists of three systems, as depicted in Fig. 1, details of which are given in Table I. Alternative equipment may be employed for regulating the nitrogen and reducing the pressure, but compliance with the details given for the distillation system is important.

3.1 Nitrogen Regulation System

Referring to Fig. 1, the gas jar "D" contains a MIL-L-23699 type synthetic fluid, which, with the teepee "K", serves as a safety valve by preventing excessive pressure build-up in the glass distillation system should the nitrogen, supplied from a cylinder of the gas, be left on when the system is not open to atmosphere. The nitrogen is supplied to the teepee somewhat in excess of that required for the distillation system, the excess overcoming the head of fluid outside the teepee and escaping to atmosphere.

During the "stripping" operation, nitrogen is admitted to the distillation system by closing s1, s2, s3 and opening s4, s5 and the needle valve "V" of the rotameter "F". The restricted area of the needle valve ensures that the gas, upon entering the test sample in "A" via the delivery tube 1, has by then expanded to the low pressure in the system, thereby obviating any need for a restriction at the end of the delivery tube which would be less effective in preventing excessive turbulence of the test sample.

Should the nitrogen supply to the regulation system fail or, due to other circumstances, the excess at the teepee fall below that demanded by the reduced pressure in the distillation system, fluid will be drawn from the gas jar into the trap "E", which serves the purpose of protecting the rotameter against contamination by the fluid. Fluid in the trap may be returned to the gas jar by opening s1, s3 and closing s5 and s4, thereby avoiding the inconvenience of disconnecting the trap.

Upon completion of the "stripping" operation, sufficient nitrogen must be allowed to enter the distillation system to restore the pressure therein to substantially atmospheric, an operation which is somewhat time-consuming owing to the restriction in flow through the rotameter needle valve even when the latter is fully opened. The operation may be hastened by opening s1, s2 and then, after ensuring that s4 remains open to prevent excessive pressure build-up, closing s3, which enables the nitrogen to by-pass the needle valve.

Included in the nitrogen regulation system is a Quickfit connector c1 which enables the distillation system to be readily disconnected and reconnected.

3.2 Pressure Reducing System

The pressure reducing system in Fig. 1 consists of a mechanical vacuum pump "P", McLeod pressure gauge "G" and screw clips "s6, s7".

The pump speed cannot be varied, and the pump should, therefore, be capable of reducing the pressure below that actually required during a determination. The requisite pressure is obtained and maintained by opening s7 slightly to admit slow leakage of air to the pump inlet. This also eliminates pressure pulsations and thereby ensures a steady rotameter reading.

Upon completion of the "stripping" operation, the distillation system is isolated from the pump by closing s6, following which s7 is opened fully to atmosphere before switching off the pump so that no pump oil is sucked back.

Included in the pressure reducing system is a Quickfit connector c2, which enables the distillation system to be readily disconnected and reconnected.

3.3 Distillation System

Referring to Fig. 1, the flask "A", stillhead recovery bend "H", condenser "C", vacuum connection bend "J" and receiver "B" consist of Corning Quickfit glassware. The nitrogen delivery tube "I" and the thermometer "t" are fitted to the sockets of the flask "A" by means of Quickfit cone/screwthread adapters.

The flask "A" rests upon asbestos-covered gauze, supported by tripod "T", and the heat source is a treble Bunsen burner "U". Surrounding "A" is a cylindrical heat insulator "S", the height of which can be adjusted by means of three screwthread legs. The lid "L" of the insulator consists of two semi-circular pieces of Maronite in which are cut semi-circular holes (see drawing No. 2348) through which the necks of the flask "A" protrude. Part of the stillhead recovery bend lies within the space enclosed by a maronite heat insulator "R", the two halves of which are held together by an internal spring to facilitate removal upon completion of the "stripping" operation (see drawing No. 2349). Vapour evolved from volatile contaminants is prevented from condensing back into "A" by means of the hot gases convected upwards over "A" and through the cavity of the insulator "R".

4. Procedure

- 4.1 Set up the apparatus as in Fig. 1 using glass and heavy-wall rubber tubing for connecting the components of the nitrogen regulation and pressure reducing systems. Seal the ground-glass joints of the distillation system with the minimum of vacuum grease, and adjust the nitrogen delivery tube "I" so as to leave 12 ± 2 mm. clearance between its extremity, measured along the axis of the tube, and the bottom of the flask "A". Adjust the thermometer so that the bottom of its bulb lies 12 ± 2 mm. above the bottom of the flask, and introduce into the gas jar approximately 1500 ml. of a MIL-L-23699 type synthetic fluid so that the long limb of the teepiece "K" is immersed to a depth of 225 ± 5 mm.

- 4.2 Ensure that the apparatus is leakproof by closing s1, s3, s5, opening "V" fully, and exhausting to 1 Torr or less. Successive pressure measurements taken after closing s6, opening s7 and switching off the pump should remain steady with no tendency to increase.
- 4.3 Disconnect the distillation flask assembly from the connector c1 and the condenser, and without removing the stillhead recovery bend from the flask, carefully wipe off all vacuum grease from the groundglass cone. Weigh the assembly to the nearest 0.1 g, and denote the weight by W_1 (Note 1).
- 4.4 Remove the thermometer assembly from the socket of the distillation flask, and place it where the greased cone cannot come into contact with other materials.* By means of a glass funnel, the stem of which must not be allowed to come into contact with the greased surface of the flask socket, introduce into the flask 450 ± 10 ml. of the test sample. Allow the funnel to drain and then remove it from the flask, taking care to avoid contact of the stem and any adhering test sample with the greased socket. Replace the thermometer assembly, weigh to the nearest 0.1 g and denote the weight by W_2 (Note 1).
- 4.5 Re-grease the cone of the stillhead recovery bend, and re-connect the distillation flask assembly to the nitrogen regulation and pressure reducing systems. Close all screw clips and the rotameter valve.
- 4.6 Open s4, s5 and turn on the nitrogen supply to produce a good excess to the teepee. Open s6, s7 and open the rotameter valve sufficiently to produce a flow of approximately 6L/Hr. (see Note 2). Next, switch on the pump and close s7 sufficiently to maintain a pressure of 8 to 12 Torr McLeod reading while maintaining a nitrogen flow of 2 to 4 L/Hr. by re-adjustment of the rotameter valve (see Note 3). Upon closing s7, ensure that fluid in the gas jar is not drawn over into the trap "E" by increasing the supply of nitrogen to the teepee if necessary (see Note 4).
- 4.7 Apply sufficient heat from the treble Bunsen to raise the temperature of the test sample, as indicated by the thermometer "t", to 195°C in 23 ± 7 minutes, taking care not to overshoot 195°C by removing the Bunsen when the thermometer indicates 179°C (see Note 5). Maintain the temperature between 185°C and 195°C until condensate dripping off the end of the stillhead recovery bend falls below 3 drops/minute, (1 drop in 20 seconds). Should the temperature fall to 185°C before this end-point is reached, re-apply heat from the Bunsen until the temperature commences to rise again.

* A one litre beaker is useful for this purpose.

- 4.8 Close s6, open s7 fully, switch off the pump, and then immediately carry out the procedure below under 4.9.
- 4.9 Increase the excess of nitrogen to the tee piece and open the rotameter valve fully. When the rotameter reading has fallen below 1.5 L/Hr., open s1, s2 and close the rotameter valve after ensuring that s4 remains open to bring the pressure in the system up to atmospheric more quickly while safeguarding against excessive pressure build-up. Allow the temperature to fall below 80°C or lower the temperature by forced cooling by connecting the Bunsen to a compressed air supply and then, with the nitrogen still on, carefully disconnect the nitrogen regulation system by means of the connector c1 and immediately open s6 (see Note 6). Finally, turn off the nitrogen.
- 4.10 Repeat the procedure under 4.3, but denote the weight of the distillation flask assembly and "stripped" sample by W_3 (see Note 1).
- 4.11 Remove the sample from the flask by the procedure below under 4.12, which eliminates any possibility of contaminating the sample by vacuum grease from the flask socket.
- 4.12 Re-connect the distillation flask assembly to the nitrogen regulation and pressure reducing systems. Remove the thermometer from the screwthread adaptor and replace it by the inverted U-bend illustrated in drawing No. 2350 so that the shorter limb reaches to the bottom of the flask.* Place a clean receptacle for the "stripped" sample under the longer limb, close s6, open s4, s2, s1 and turn on the nitrogen to displace the sample from the flask into the receptacle.

5. Calculating and Reporting

Calculate the volatile contaminant content (VCC) from:-

$$\text{VCC \% w/w} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

Report as less than 0.1% for values less than 0.1%.
 Report to the nearest 0.1% for values of 0.1 to 9%.
 Report to the nearest 1% for values above 9%.

* Alternatively, the U-bend may be equipped with a screwthread adaptor so that the thermometer with its screwthread may be removed without disturbing the position of the thermometer in the adaptor for subsequent use of the apparatus.

Notes

- 1 ... Omit the weighing operation if the sample is to be stripped of volatile contaminant without determination of the amount present.
- 2 ... Commencing the flow of nitrogen through the sample before the pressure in the distillation system is lowered ensures smooth release of dissolved air which otherwise may attain a state of supersaturation followed by sudden release with violent "bumping" of the sample.
- 3 ... Adjustment of s7 may be accompanied by transient pressure rises in the distillation system causing sample to ascend the nitrogen delivery tube. This may be combatted by immediately placing the finger momentarily over the open end of the rubber tube supporting s7, and which will re-establish steady nitrogen flow through the sample. The opening and/or closing of s7 should be performed in small increments at a time as otherwise insufficient time may be available to effectively apply the foregoing preventive artifice before sample is displaced up and out of the delivery tube.
- 4 ... Should fluid in the gas jar be drawn into the trap, it may be returned to the gas jar as described under 3.1 (Nitrogen Regulation System).
- 5 ... A temperature increase of about 16°C may be expected due to heat soak-back upon removing the Bunsen.
- 6 ... The system should be opened to atmosphere by firstly disconnecting c1 to prevent displacement of the sample up the delivery tube, which will occur if the system pressure happens to be less than atmospheric upon opening s6. A slight excess of nitrogen pressure in the system will produce the same effect if s6 is not opened immediately after disconnecting c1.
- 7 ... The apparatus described employs screw clips on rubber tubing to minimise cost. The precautions referred to in Notes 3 and 6 could be disregarded if a glass non-return valve were incorporated about half-way up in the delivery tube "I", and the trap "E" could be eliminated by incorporating a similar valve about half-way up in the long limb of the tee-piece "K". Substitution of screw clips s6 and s7 by quick-action valves would also facilitate operation of the apparatus.

TABLE I

Apparatus and Materials

Legend Reference in Fig. 1	Description
<u>Nitrogen Regulation System</u>	
D	Pyrex Gas Jar, height 60 mm, i/d approximately 800 mm
K	Glass Tee-piece, o/d 7mm to 8.5 mm, long limb 540 mm, each short limb 70 mm
E	Pyrex Büchner heavy-wall filter flask, nominal capacity 2000 ml, bulb dia. 170 mm, neck i/d 40 mm, overall height 275 mm. Cat. No. 1170/10 - Corning Limited
F	Rotameter No. 1100, range 0 to 6 litres/hr. air @ 15°C and 760 torr absolute. GEC-Elliott, Process Instruments Limited or Rotameter Manufacturing Company Limited, Croydon, U.K.
s1, s2, s3, s4, s5	Screw clips on rubber tubing connections of approximately i/d 4 mm, o/d 12 mm
c1	Quickfit straight connector, thread size 18, 7 to 8.5 mm, length approximately 80 mm. Cat. No. SQ4/18 - Corning Limited
<u>Distillation System</u>	
A	Quickfit flask, round bottom, three necks - centre neck and two angled necks (axis of side necks meet with axis of centre neck at bottom of flask). Nominal capacity 1000 ml. Centre socket 24/29, side sockets 19/26. Approximate overall height 180 mm. Cat. No. FR1L/3S/22A, Corning Limited.

Legend Reference in Fig. 1	Description
I (+ connection)	Nitrogen Delivery Tube o/d 7 mm to 8.5 mm fitted to flask A by means of Quickfit cone/screwthread straight adaptor, thread size 18, 7 to 8.5 mm, cone size 19/26. Cat. No. ST52/18 - Corning Limited
t	Mercury filled Celsius Scale Thermometer, 75 mm immersion. Scale range 0 to 250°C in 1°C divisions figured @ 10°C intervals. Product No. 40-410 - Brannan Thermometers, U.K.
t - connection	Thermometer t fitted to flask A by means of Quickfit cone/screwthread straight adaptor, thread size 13, 6 to 7 mm, cone size 24/19. Cat. No. ST53/13 - Corning Limited
H	Quickfit Stillhead Recovery Bend, sloping. Both cone sizes 19/26 to fit flask A and condenser C. Cat. No. SH1/22 - Corning Limited
C	Quickfit Double Surface Condenser (Davies). Socket size 19/26, Cone size 19/26. Approximate overall length 340 mm. Cat. No. C5/22 - Corning Limited
J	Quickfit Bend with Vacuum Connection. Socket size 19/26. Approximate overall length 130 mm. Cat. No. RA3/22 - Corning Limited
B	Quickfit Flask, round bottom, short neck, nominal capacity 1000 ml, socket size 19/26. Approximate overall height 175 mm. Approximate neck length 15 mm. Cat. No. FRIL/25 - Corning Limited
T	Circular Tripod, o/d 180 mm, i/d 170 mm, height 250 mm, widest spacing of legs 200 mm maximum
S	Cylindrical Heat Insulator. As per drawing No. 2347
L	Lid of Heat Insulator S. As per drawing No. 2348
R	Stillhead Heat Insulator. As per drawing No. 2349

Legend Reference in Fig. 1	Description
U	Flamefast Treble Bunsen Burner. Cat. No. 281/0216 - Baird & Tatlock, U.K.
<u>Pressure Reducing System</u>	
P	Mechanical, rotary, oil-sealed, vane-type, two-stage vacuum pump, ultimate pressure 1×10^4 Torr (McLeod), free air displacement 140 litres/min. Cat. No. 1402 - Sargent-Welch Scientific Company, U.S.A.
G	McLeod Pressure Gauge or equivalent with scale minimum equivalent to 0.1 Torr or less
s6, s7	Screw clips on rubber tubing connections of approximately i/d 4 mm, o/d 12 mm.
c2	Quickfit straight connector, thread size 18, 7 to 8.5 mm, length approximately 80 mm. Cat. No. SQ4/18 - Corning Limited
<u>Accessories</u>	
-	MIL-L-23699 type synthetic lubricant
-	Pyrex funnel, 100 mm diameter, stem 70 to 80 mm length
-	Asbestos covered gauze, 150 mm x 150 mm, corners bent down over tripod T
-	Rubber tubing of approximate i/d 4 mm, approximate o/d 12 mm, glass tubing o/d 7 to 8.5 mm and teepieces and Y-pieces for connecting components of nitrogen regulation and pressure reducing systems
-	Vacuum grease, ASTM penetrometer dial reading approximately 150, melting point not less than 90°C
-	Inverted U-Bend. As per drawing No. 2350

Legend
Reference
in Fig. 1

Description

-	Supply of "White Spot" Nitrogen
---	---------------------------------

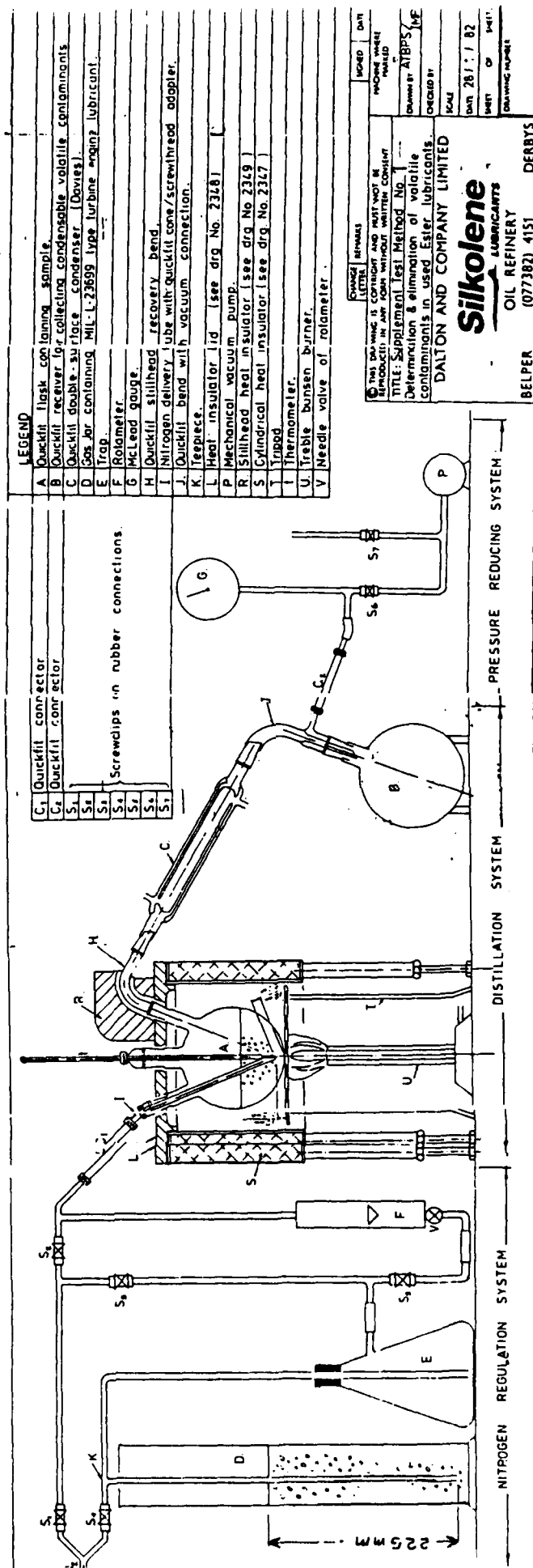
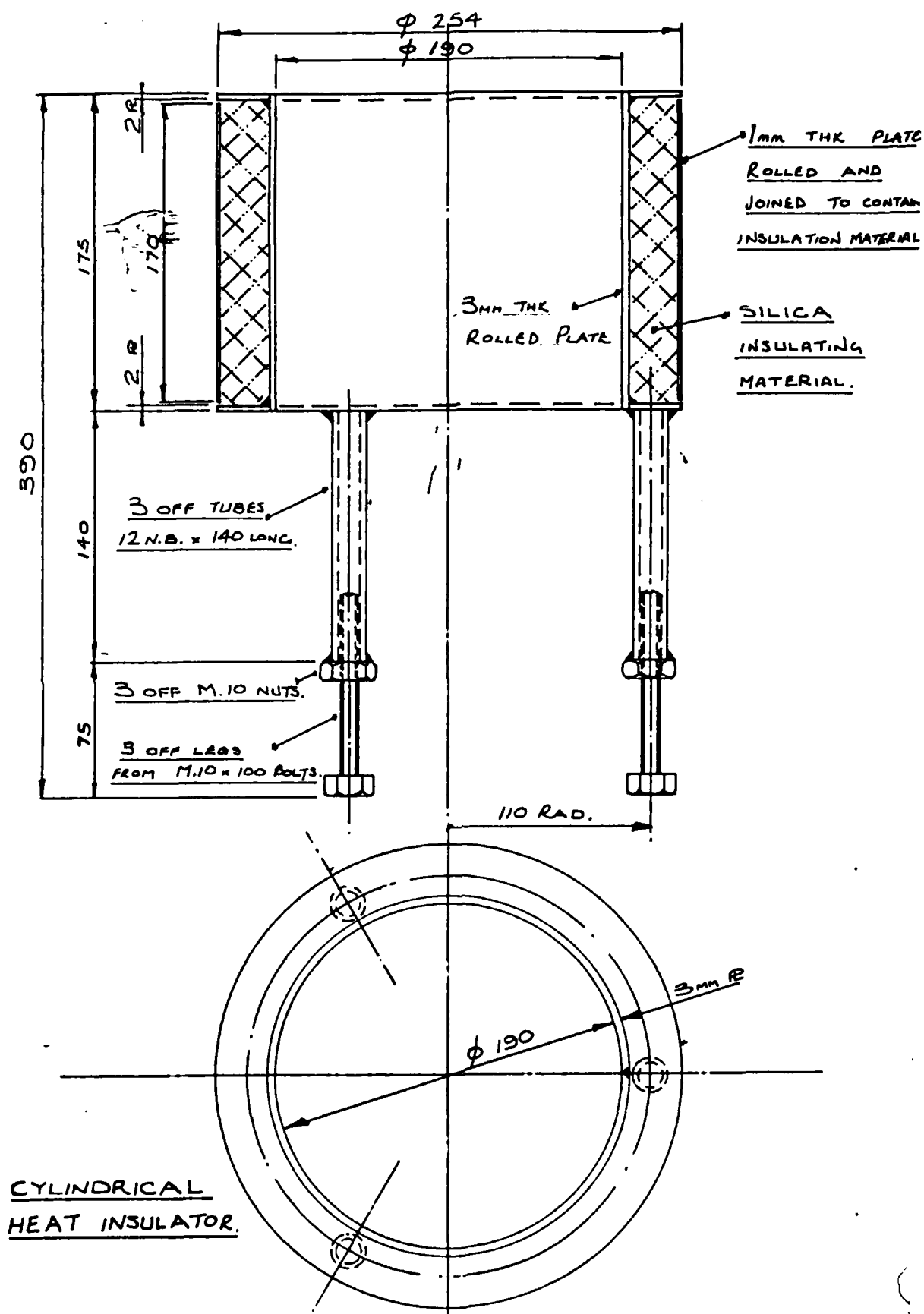
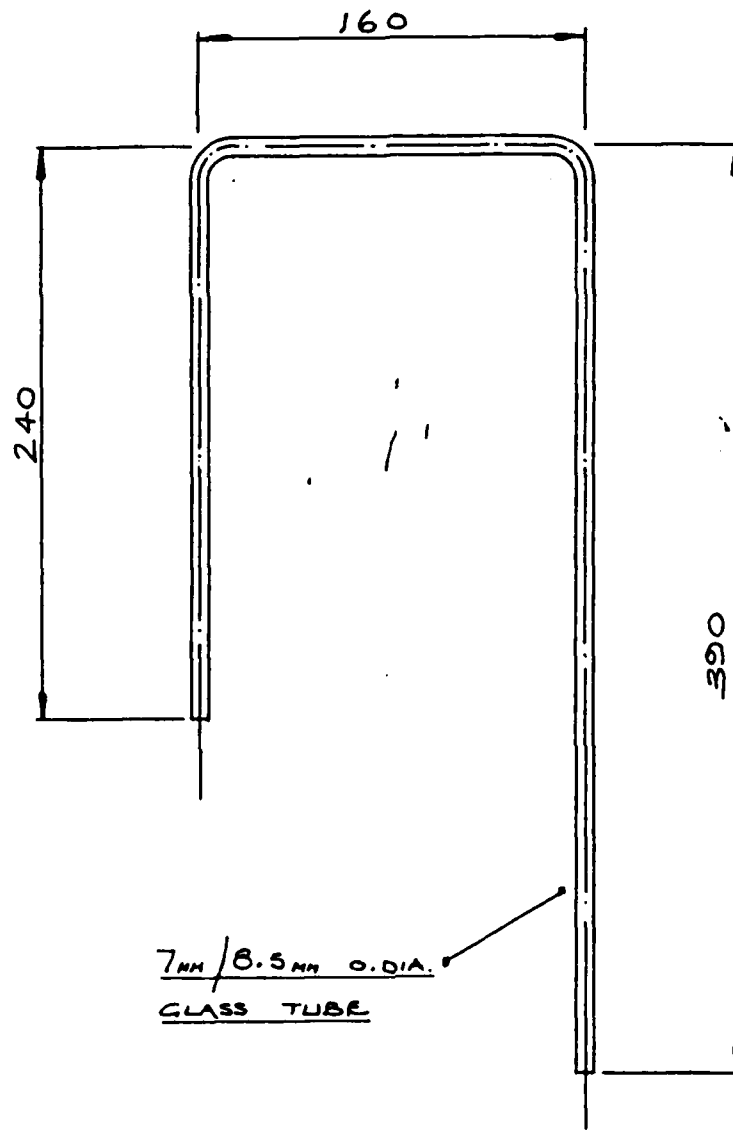


Fig. 1 - STM No. 1: General View of Assembled Equipment



DRG. No. 2347 - STM No. 1: Specification for Cylindrical Heat Insulator



DRG. No. 2350 - STM No.1: Specification for Inverted U-Bend

Appendix B

Supplement Test Method No. 2

Determination of Volatile Hydrocarbon Content of Used Synthetic Turbine Engine Lubricant

1. Introduction

The method is intended for determining, by gas liquid chromatography (GLC), the volatile hydrocarbon contents of used diester and polyol ester turbine engine lubricants in the absence of non-hydrocarbon volatile contaminants excepting moisture.

Volatile hydrocarbons are defined herein as those hydrocarbon contaminants in used ester type turbine engine lubricants which are more volatile than n-hexadecane boiling @ 287°C. Examples are Avcat, Avtur and Avtag kerosene type turbine fuels, domestic paraffin, stoddard solvent and other petroleum naphthas.

The method is not suitable for determination of non-hydrocarbon volatile contaminants, the presence of which, excepting moisture, give rise to higher results for volatile hydrocarbon content than the true value. The magnitude of the error depends upon the concentrations of the non-hydrocarbon volatile contaminants and their GLC response factors, which, in the case of contaminants such as trichloroethane, methanol and other low boiling alcohols, are lower than the hydrocarbon response factor. 3 percent trichloroethane, for example, would increase the determined result for volatile hydrocarbon content by 1 percent.

2. Summary of Method

An aliquot of the test sample is blended with a measured proportion of n-hexadecane, which serves as an internal standard and marker. 1 µl of the blend is injected into the capillary column of a gas chromatograph, which is operated under conditions producing a well-defined peak for n-hexadecane, and one or a few peaks for volatile hydrocarbons which elute ahead of the n-hexadecane.

The volatile hydrocarbon content is calculated from the areas under the peaks of the chromatogram, and the known concentration of n-hexadecane in the blend.

3. Apparatus and Materials

3.1 Gas chromatograph incorporating split/splitless injector, flame

ionisation detector, 5 m OV101 capillary column and integration facility (Note 1).

- 3.2 1 μ l syringe.
- 3.3 1 ml graduated pipette
- 3.4 25 ml volumetric flask
- 3.5 250 ml beaker
- 3.6 Glass pouring rod
- 3.7 Analytical balance
- 3.8 Vacuum dessicator (optional).
- 3.9 n-hexadecane, 99% purity, mp. 18°C, bp. 287°C, $n_D^{20} = 1.4335$ (Note 2).

4. Procedure

- 4.1 Weigh the 25 ml volumetric flask, and denote the weight by W_1 . Pipette into the flask 0.25 ml of the hexadecane standard, re-weigh and denote the weight by W_2 .
- 4.2 Ensure by thorough shaking or other means of agitation that the test sample is homogeneous, and then transfer approximately 30 ml into the 250 ml beaker to facilitate subsequent manipulation.
- 4.3 With the aid of the pouring rod, fill the volumetric flask containing the hexadecane to the mark with test sample from the 250 ml beaker. Re-weigh the flask and contents, and denote the weight by W_3 . Stopper the flask, shake thoroughly and then allow all air bubbles to escape from the liquid (Note 3).
- 4.4 Ensure that the GLC equipment is set up to operate under optimum conditions (Note 4).
- 4.5 Open the splitter valve, inject 1 μ l of the spiked sample by means of the syringe, and close the valve about 1 minute after injection.

- 4.6 Measure, on the resulting chromatogram, the areas under the peaks produced by components which eluted ahead of the hexadecane, and measure also the area under the hexadecane peak (Note 5).
- 4.7 Continue to operate the gas chromatograph under the same conditions until all the lubricant has eluted (Note 6).

5. Calculating and Reporting

Calculate the volatile hydrocarbon content (VHC) from:-

$$\text{VHC \% w/w} = \frac{A_{\text{VHC}}}{A_{\text{H}}} \times C_{\text{H}}$$

Where A_{VHC} = Summation of areas under peaks produced by components eluting ahead of n-hexadecane.

A_{H} = Area under n-hexadecane peak.

C_{H} = Concentration % w/w of n-hexadecane in spiked sample.

$$= \frac{W_2 - W_1}{W_3 - W_1} \times 100$$

Report as less than 0.1 percent for values less than 0.1 percent.

Report to the nearest 0.1 percent for values of 0.1 to 2 percent.

Report to the nearest 1 percent for values between 2 and 10 percent.

Report as greater than 10 percent for values of 10 percent or over.

Notes

- 1 ... A Perkin-Elmer Sigma 115 gas chromatograph with basic facility was utilised in developing the present method. The programme for the method is given in Fig. 1, and by way of an example, the print-out obtained for a sample of used turbine engine lubricant coded OP-232-1 by AFAPL is given in Fig. 2.
- 2 ... The purity of the n-hexadecane is important. A source of suitable material is Aldrich Chemical Company Limited, Dorset, U.K., who have locations in the U.S.A.
- 3 ... Release of entrained air may be hastened by placing the un-stoppered flask in a vacuum dessicator and reducing the pressure. This is not advised for samples containing very volatile hydrocarbons as a proportion might be lost when under low pressure.
- 4 ... Because of the variable nature of gas chromatographic equipment and columns, it is left to the discretion of the operator to optimise the conditions for his particular equipment. Conditions found suitable for the gas chromatograph cited in Note 1 were:-

Column	-	5 m OV101
Detector	-	FID @ 300°C
Air Pressure	-	30 psi
Carrier Gas	-	N ₂ @ 20 psi
Injector	-	Wide-bore glass liner packed with SE30; temperature 300°C
Split Ratio	-	35:1
Sample Size	-	1 µl
Oven Programme	-	135°C for 2 minutes followed by increase to 300°C @ 40°C per minute. Thereafter, hold @ 300°C until all lubricant has eluted.
Range	-	10
Attenuation	-	4

The retention time for n-hexadecane under these conditions is about 0.6 minutes.

- 5 ... The peak areas are best calculated by electronic integration
- 6 ... A "burn-out" time of 25 to 60 minutes will usually be found to elute all the lubricant.

```

/BL UHC
5  REM ** INITIALISE VARIABLES **
10  DIM P$(15),A$(20)
20  LET M=1
30  LET S=0
40  LET E=20
50  OPEN "PP"
100 REM ** INPUT AND CHECK DATA **
110 PRINT "FILE";
120 INPUT F1
130 IF F1=0 THEN 200
140 FID F1,I,R,A,D,P$,H,M1,M2,D1,V,W,T1,T2
150 IF I=1 THEN 200
160 IF I=0 THEN PRINT "NO SUCH FILE"
170 IF I=3 THEN PRINT "NOT A PEAK FILE"
180 PRINT "RE-INPUT FILE";
190 GOTO 120
200 PRINT "WT C16";
210 INPUT L
220 PRINT "WT OIL + C16";
230 INPUT Z
240 IF F1<>0 THEN 410
250 PRINT "NAME";
260 INPUT P$
270 CLOSE "PP"
300 REM ** SET UP GC AND RUN SAMPLE **
310 SETUP P$,1,1,1,1,M
320 RUN P$,1
330 FILE P$,1,1,F1,F2
340 IF F1=-2 THEN 300
400 REM ** GET FILE, CALCULATE AREAS AND PRINT LIST **
410 PKREP P$,F1,M
420 OPEN "PP"
430 PKPRINT P$,1
440 PRINT TAB(10); "TIME"; TAB(20); "AREA"; TAB(30); "NAME"
450 LET T=0
460 LET H=0
470 PKNEXT P$,1,A1,A2,A3,A4,A5,A6,A$
480 IF I=1 THEN 520
490 IF A$="" THEN IF H<>0 THEN LET A$="NOT SPECIFIED"
500 IF A$="" THEN LET A$="CONTAMINANT"
510 PRINT TAB(9);A1;TAB(19);A2;TAB(30);A$
520 ON I GOTO 610,540,470,530
530 IF A1>5 THEN IF A1<=E THEN LET T=T+A2
540 IF I=2 THEN LET H=H+A2
550 IF H<>0 THEN LET E=A1
560 GOTO 470
600 REM ** CALCULATE UHC AND PRINT RESULTS **
610 PRINT
620 PRINT "TOTAL AREA OF GROUP= ";T
630 PRINT "TOTAL AREA OF STANDARD= ";H
640 LET Y=T*L*100/H/Z
650 IF Y<.1 THEN PRINT "TOTAL UHC OF ";P$;"<.1%"
660 IF Y>=.1 THEN IF Y<2 THEN LET X=INT (Y*10+.5)/10
670 IF Y>=2 THEN IF Y<=10 THEN LET X=INT(Y+.5)
680 IF Y>10 THEN PRINT "TOTAL UHC OF ";P$;">10%"
690 IF Y>=.1 THEN IF Y<=10 THEN PRINT "TOTAL UHC OF ";P$;"=";X;"%"
700 PKREP P$
710 SETUP P$
720 PRINT
730 PRINT
740 GOTO 110
800 SETUP P$

```

Fig. 1 - Basic Facility Programme for Application of Perkin Elmer-Sigma 115 Gas Chromatograph to Determination of VHC by STM No. 2

EXAMPLE OF RUN:

/9R UHC.1
 PROGRAM 26
 OK
 26 : 1
 FILE?0
 WT C167.1929
 WT OIL + C16723.6063
 NAME?OP 232 1

ANAL 1 DET 1 METH 1 1 FILE 11

RUN 1 OP 232 1

SENSITIVITIES 820 40

26 : 1
 $T_R = 0.09$
 $T_R = 1.04$
 8ND6
 $T_R = 0.56$

ANAL 1 DET 1 METH 1 FILE 11
 RUN 1 OP 232 1 22 : 59.7 0 / 11 / 0

TIME	AREA	NAME
.89	.7956	CONTAMINANT
.56	4.23	HEXADECANE
1.84	.1814	NOT SPECIFIED

TOTAL AREA OF GROUP= .7956
 TOTAL AREA OF STANDARD= 4.23
 TOTAL UHC OF OP 232 1= .2 %

Fig. 2 - Perkin-Elmer Sigma 115 Gas Chromatograph Print-Out for Used Turbine Engine Lubricant OP-232-1 Containing Hexadecane as Marker and Internal Standard

APPENDIX C

Supplement Test Method No. 3

Determination of Mineral Oil Content of Used Synthetic Turbine Engine Lubricant

1. Scope

The method is intended for determining, in used diester and/or polyol ester turbine engine lubricants, concentrations of paraffinic and/or naphthenic type mineral oils exceeding 3% w/w. The method is not suitable for determining mineral oil concentrations of 3% or less.

2. Outline of Method

The method is based upon thin-layer chromatography using a saturated solution of dimethyl sulphoxide in cyclohexane as eluent, and a 20% solution of antimony pentachloride in carbon tetrachloride as reagent for the chromatogram.

The mineral oil content is adjudged by comparing the intensity of the reaction spot with those produced in parallel by standard solutions of mineral oil in di-iso-octyl Azelate.

3. Apparatus and Procedure

The test shall be carried out in accordance with Rolls-Royce Method 1032 Issue 1, details of which are attached hereto, but the mineral oil standards employed shall be as specified below.

Two spots are obtained in the presence of mineral oil. The spots utilised in comparing the test sample results with those of the standards shall have an R_f value within the range 0.4 to 0.6.

Should the method indicate a mineral oil content greater than 6% w/w, repeat the test on an aliquot of the test sample diluted with di-iso-octyl azelate, pure grade, to bring the mineral oil content between 3 and 6% w/w and correct the result obtained for the diluted sample as follows:-

$$(MO)_U = (MO)_d / F$$

where:-

$(MO)_U$ = Mineral oil content of original sample

$(MO)_d$ = Determined mineral oil content of diluted sample.

F = Fraction of original sample contained in diluted sample.

4. Mineral Oil Standards

Di-iso-octyl Azelate, pure grade, containing 3, 4, 5 and 6% w/w concentrations of mineral oil conforming to DERM 2490, Issue 2, Am. 1 - OM 11 (NATO-O-135).

ATTACHMENT TO SUPPLEMENT TEST METHOD NO. 3

Rolls-Royce Method 1032 Issue 1

Application of Thin Layer Chromatography to Gas Turbine Lubricants

Introduction

Thin layer chromatography (TLC) provides a cheap and rapid analytical technique which has been found to be particularly useful for the identification, and in some instances, the estimation of additives and contaminants in gas turbine lubricants.

Gas turbine lubricants in general contain more than one additive, some of which may be common to a number of lubricants, while one or more of the others, if detectable, will serve as a basis for identification of a specific lubricant. The merit of TLC for this purpose lies in the readiness with which such additives may be separated and identified with an exceedingly small sample.

The procedure which has been adopted in the present method for the preparation of the chromatogram is described in detail in so far as this can be generalised. Specific details relevant to the material under identification are given in the Tables below, which will be updated as and when techniques for other materials warrant inclusion.

Scope

The procedure is applicable to gas turbine lubricants, and is suitable for the identification, and where indicated, the estimation of the materials listed in Table (i).

Definitions

Terms and definitions employed in the present method are as follows:-

Carrier Plate

Support for the adsorbent.

Adsorbent

The material employed as a stationary phase in the form of a thin layer on the carrier plate.

Starting Line

A line marked across the TLC plate upon which the sample drop is applied, and which serves as the datum from which the R_f-value is measured.

Solvent

The fluid employed for elution of the sample drop on the TLC plate.

Solvent Front

The distance of the solvent rise, measured from the starting line.

Chromatogram

The visual result produced upon the TLC plate upon treatment of the eluted sample with reagent.

Spot

A stain on the chromatogram representing the coloured reaction product of a separated component with the reagent employed.

Rf-Value

The ratio of the distance of the centre of the coloured spot, measured from the starting line to the solvent front.

Outline of Method

The method comprises the application of orthodox TLC techniques, using the "ascending development" method.

Apparatus Required

TLC Plate

Carrier plates in any suitable material such as glass, plastics or aluminium foil may be employed, but the height of the plate shall be 20 cm.

The adsorbent, and film thickness thereof, shall be as given in Table (i).

The TLC plates may be prepared (1)* in the laboratory, using a suitable leveller and spreader, drying rack and desiccant cabinet, 30 minutes activation at 130°C, being necessary prior to use.

Alternatively, TLC plates ready for use may be purchased from a reputable thin-layer equipment supply house (2), this in general being more convenient and less costly.

* Number in parentheses designate References at end of method.

Drop Positioning Template

One of the many templates commercially available may be used for spacing the sample drops along the starting line.

Microlitre Sample Injector

A microlitre syringe shall be used for transferring to the TLC plate sample drops less than 5 μ l, otherwise a microlitre pipette may be used for drops of 5 or 10 μ l.

Elution Tank

The elution tank shall consist of a seamless glass vessel with lipped flange and ground lid, and capable of holding the TLC plate in a vertical or near vertical position. The volume of the tank shall be as small as possible for the size and number of plates eluted simultaneously, and may be obtained from one of the many supply houses handling thin-layer equipment.

Reagent Sprayer

Any simple spraying device capable of producing an aerosol may be employed; a laboratory spray gun utilising dichloro-difluoromethane propellant is convenient.

Ultra Violet Fluorescence Lamp

A source of ultra violet radiation for excitation of the eluted TLC plate and/or examination of the chromatogram will be required where specified in Table (i); commercial multi-purpose equipment providing uniform high-intensity 254 and 366 m μ radiation, and visible light visualisation, is convenient.

Reagents Required

The reagents, designated by numbers in Table (i), are described in detail in Table (ii), which also covers standards of comparison where applicable.

Procedure

The sample or samples under examination shall be applied to the TLC plate in the appropriate quantity by means of the injector, after having scribed on the plate the specified solvent front, using the template to position the drops and starting line.

The TLC plate or plates shall next be placed to a depth of 0.5 to 1.0 cm in the solvent previously introduced into the clean elution tank which, unless otherwise specified in Table (i), shall not be lined. The lid of the tank shall then be replaced immediately and, after having allowed the solvent to rise to the scribed front, the plate or plates

shall be removed and allowed to dry in a vertical position.

The separation of some materials can be improved by multiple elution, which may involve different solvents; these are given in Table (i) where appropriate.

The dried TLC plate, after having been viewed under ultra violet radiation where necessary, shall next be sprayed* with the specified reagent or reagents in the sequence given in Table (i). It is important that the spray be as fine as possible and, especially for quantitative work, that it be applied in even density; the specific procedure employed by D. Waldi (1, p.484) is recommended. The duration of spraying is indicated in Table (i). When development of the spot occurs instantaneously, careful inspection of the chromatogram after each pass with the sprayer will indicate when to stop, care being taken not to overspray as this causes spreading of the spot, and staining of the background.

Finally, the chromatogram shall be examined for spot colour and Rf-value for identification purposes. The concentration of the identified material shall be estimated, where applicable in Table (i), by comparison of the colour intensity of the spot with those of the spots produced upon running in parallel on the same TLC plate the standards of comparison given in Table (ii).

Calculating and Reporting

The colours and Rf-value of the spots and ultra violet fluorescence of the eluted sample and chromatogram, shall be reported when the identity of the material giving rise to the chromatogram is unknown, Rf-value being given by:-

$$\text{Rf-Value} = \frac{\text{Spot Centre Distance from Starting Line}}{\text{Solvent Front}}$$

The centre of the spot, regardless of the shape of the spot which may not be always truly circular, shall be adjudged as the centre of the area of highest colour intensity.

The concentration of identified material shall be reported to an accuracy having the range of the difference between the two nearest standards employed.

* WARNING

All spraying operations must be carried out in a fume cupboard with adequate extraction, a sheet of paper placed between the TLC plate and the walls of the cupboard preventing attack by corrosive reagents.

REFERENCES

- (1) E. Stahl - Thin-Layer Chromatography.
Pub., Academic Press, New York and London.
- (2) E. Merck AG Darmstadt, Germany.
(U.K. Distributors: Anderman & Company Limited, London).
- (3) Shell Research Centre, Thornton.
Details provided by private communication.
- (4) Texaco Inc., Beacon, N.Y.
Solvent details provided by private communication.
- (5) Dalton & Company Limited, Belper, Derbyshire.
Details provided by private communication.
- (6) Castrol Research Laboratories, Bracknell, Berkshire.
Modification of Bracknell Experimental Method No. 12
comprising unlined tank and *different reagent*.

RR Method 1032, Issue 1 - Application of Thin Layer Chromatography to Gas Turbine Lubricants

Table (i)

Component or Contaminant	Absorbent and film Thickness	Sample Drop Size (μl)	Solvent and No. of Elutions	Solvent Front (cm)	Reaction			Spot Description	Rf-Value x 100	Applicable Concentration Range (%)	Remarks
					Reagent	Spraying Duration	Reaction Time				
Phenothiazine (PTZ)	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Orange crescent - heavy tailing	47 - 54	0.5 - 1.0	(3)
Phenyl β-Naphthylamine (FBN)	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Grey-slight tailing	54	0.75 - 1.25	(3)
Octyl β-Naphthylamine (ONB)	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Green	55	0.8 - 1.5	Eluted sample-green under U.V.
3,7, Dioctyl Phenothiazine (DOPT)	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Bright orange/red	58 - 60	0.5 - 1.5	(3)
Diphenylamine	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Mid blue/purple	56 - 63	-	(3)
Phenyl-β-Naphthylamine (PAN)	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Deep blue - slight tailing	58 - 64	0.5 - 1.5	Eluted sample-blue under U.V.
Di Octyl Di phenyl amine (DOPT)	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Deep green	71 - 80	1.0 - 4.0	(3)
N-Benzyl 3,7 Dioctyl Phenothiazine	Kieselgel F ₂₅₄ 250μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Deep purple - heavy tailing	88 - 90	0.5 - 2.0	(3)

Table (i) - Continued

RR Method 1032, Issue 1 - Application of Thin Layer Chromatography to Gas Turbine Lubricants

Component or Contaminant	Absorbent and film Thickness	Sample Drop Size (μ l)	Solvent and No. of Elutions	Solvent Front (cm)	Reaction			Spot Description	Rf-Value $\times 100$	Applicable Concentration Range (%)	Remarks	Refs.
					Reagent	Spraying Duration	Reaction Time					
Benztiazole (372)	Kieselgel F54 250 μ	5	40:60, Toluene:Hexane 1 elution	15	3	To max. intensity	Immediate	Faint pink ellipse	50 - 94	0.2 - 1.0		(3)
Phenothiazine -5-Oxide (sulphoxide)	Kieselgel F54 250 μ	10 (25% soln. in chloro- form)	60:90 Diethyl Ether n-Pentane	15	3	To max. intensity	Immediate	Burnt Orange	10 - 13	Not established	Lower Limit of detection = 0.015%	(4)

Table (i) - Concluded

RR Method 1032, Issue 1 - Application of Thin Layer Chromatography to Gas Turbine Lubricants

Component or Contaminant	Absorbent and film Thickness	Sample Drop Size (μ l)	Solvent and No. of Elutions	Solvent Front (cm)	Reaction		Spot Description	Rf-Value $\times 100$	Applicable Concentration Range (%)	Remarks	Ref.
					Reagent	Spraying Duration					
Skydrol 500B	Kieselgel G, or Kieselgel F ₂₅₄ 250 μ	5 or 10	Methylene Dichloride 1 elution. Lined tank	15	1	Until damp. Air dry + 10 to 15 mins. @ 130°C.				Quantitative technique available. See Appendix II, 4, for standards	(5)
					2	Spray while hot to max. intensity	Almost immediate	Two orange crescents	13 - 15 31 - 34		
Mineral Oil	Kieselgel F ₂₅₄ 250 μ	5	Sat. soln. Dimethyl Sulphoxide in cyclohexane 1 elution	15	3	Until almost damp. Air dry + 15 mins. 100°C.	Almost immediate	Two grey/ brown diffuse stains	40 - 60	Quantitative technique available. See Appendix II, 5, for standards	(6)

TABLE (ii)

Reagents and Standard Solutions

<u>Reagent</u>	<u>Preparation</u>
1	<u>Ethanolic KOH</u> 1 g KOH, analytical grade, dissolved in 0.5 ml water and diluted with 20 ml ethanol
2	<u>Diazotised p-nitro aniline</u> a) 1 g p-nitro aniline dissolved in 10 ml cold conc. HCl and diluted with 250 ml distilled water b) 5 g NaNO_2 dissolved in 100 ml distilled water Mix a) and b), equal volumes, at 0°C immediately before use
3	<u>Antimony Pentachloride</u> 20% solution of SbCl_5 in CCl_4 prepared immediately before use (Avoid skin contact and protect eyes)
4	<u>Skydrol 500B Standards</u> Di-octyl Sebacate pure grade, containing 0.1, 0.3, 0.5 and 1% w/w Skydrol 500B
5	<u>Mineral Oil Standards</u> Di-iso-Octyl Azelate pure grade, containing 0.1, 1.0, 1.5 and 2.0% w/w concentration of DTD 44D oil

APPENDIX D TENTATIVE

Gravimetric Determination of Mineral Oil Content of Used Synthetic Turbine Engine Lubricant

1. Introduction

The method was intended for the determination of mineral oil in concentrations of 1% w/w or more in used polyol ester and diester turbine engine lubricants after removal of volatile contaminants.

The method should be regarded as tentative until sufficient experience in its application has been gained.

Inhibitor systems and load-carrying agents normally found in synthetic turbine engine lubricants, and the predominance of either naphthenes or paraffins in the structure of the mineral oil content of the standard, were found to have no significant influence upon the results, but high results exceeding the mineral oil content of the test material may be expected in the presence of other non-volatile unsaponifiable matter.

2. Summary of Method

The mineral oil content is extracted by means of diethyl ether from 10 g of test material after saponification of the latter by means of aqueous/ethanolic potassium hydroxide solution, and evaporation of the latter to dryness followed by addition of water to dissolve the salts and liberated polyols.

The ether extract containing the mineral oil, and monohydric alcohols liberated from diester components of the test material, is filtered to remove insoluble matter, dried by addition of anhydrous sodium sulphate, filtered and evaporated to dryness. Mineral oil is separated from the residue by washing out monohydric alcohols by means of ethanol, and is weighed, either as such, or by deducting from the weight of the original residue the weight of residue obtained upon evaporating to dryness the ethanolic filtrate and washings.

3. Apparatus

Wide neck 250 ml Erlenmeyer flask (Note 1)
Cold water reflux condenser
Electric heating mantle
250 ml vitrosil evaporating basin
500 ml separating funnel (Note 1)
250 ml separating funnel

400 ml conical beaker
Filter-paper glass funnel
0.8 micron millipore filter
Steam bath

4. Materials

Potassium hydroxide, analar grade
Anhydrous sodium sulphate, analar grade
Diethyl ether, analar grade
Ethanol
Whatman No. 541 filter paper

5. Procedures

- 5.1 Weigh out approximately 10 g sample into a 250 ml Erlenmeyer flask (Note 1) and denote the exact weight of sample by W_1 .
- 5.2 Add a solution of 8 g potassium hydroxide in 15 ml deionised water followed by 60 ml ethanol.
- 5.3 Swirl the flask to mix the contents, connect to a cold water reflux condenser, and by means of a heating mantle, heat the flask to maintain gentle refluxing for 20 hours.
- 5.4 Transfer contents of flask to a 250 ml evaporating basin. Wash the flask three times, each with 15 ml water, and add the washings to the evaporating basin.
- 5.5 Evaporate to dryness on the steam bath.
- 5.6 Add 100 ml water, warm to dissolve salts, and transfer to a 500 ml separating funnel (Note 2). Wash the basin three times, each with 15 ml water, and transfer all the washings to the separating funnel.
- 5.7 Add 30 ml diethyl ether to the contents of the separating funnel and shake vigorously for 2 minutes, taking care to vent the funnel frequently to prevent excessive pressure build-up.
- 5.8 Allow the two liquid phases to separate completely. Immediately after separation, and if possible before any flocculent insoluble matter has had time to settle and compact itself at the bottom of the funnel (Note 2), run the aqueous layer with as much of the insoluble matter as possible into a 400 ml conical beaker. Run the ether layer into a 250 ml Erlenmeyer flask, and stopper to prevent evaporation.

- 5.9 Return the aqueous layer from the conical beaker to the separating funnel.
- 5.10 Repeat 5.7 and 5.8 three times, collecting the ether extracts in the Erlenmeyer flask containing the previous ether extract. Discard the aqueous material.
- 5.11 Filter the combined ether extracts through a Whatman No. 541 paper (Note 3) into a 250 ml separating funnel. Wash the filter three times, each with 15 ml diethyl ether, and collect the washings in the separating funnel containing the filtered ether extracts.
- 5.12 Add to the ether extracts and washings in the separating funnel approximately 10 g anhydrous sodium sulphate, and allow to stand several hours or overnight.
- 5.13 Run the dried ether extracts from the separating funnel through a Whatman No. 541 paper into a tared 250 ml evaporating basin. Wash the separating funnel three times, each with 20 ml diethyl ether, allowing each washing to pass successively through the Whatman paper into the evaporating basin.
- 5.14 Evaporate the contents of the tared evaporating basin to dryness on the steam bath. Cool in a desiccator and weigh. Denote the weight of the residue by W_2 .
- 5.15 Add 50 ml ethanol to the dried residue in the evaporating basin. Warm to approximately 50°C, and filter through a tared 0.8 micron millipore filter into a tared 250 ml evaporating basin.
- 5.16 Rinse the original evaporating basin three times, each with 50 ml ethanol and allow each rinse to pass successively through the millipore into the tared evaporating basin containing the ethanolic filtrate.
- 5.17 Dry the tared millipore filter with the mineral oil residue for 10 minutes in an air-circulating oven @ 90°C. Cool in a desiccator, and denote the weight of residue by W_3 .
- 5.18 Evaporate the ethanolic filtrate and washings in the tared evaporating basin to dryness on the water bath, and finally dry for 15 minutes in an air-circulating oven @ 90°C. Denote the weight of residue by W_4 .

6. Calculating and Reporting

Calculate the mineral oil content (MOC) from either (1) or (2) below:-

$$\text{MOC \% w/w} = \frac{W_3}{W_1} \times 100 \quad \dots \quad \dots \quad \dots \quad (1)$$

$$= \frac{W_2 - W_4}{W_1} \times 100 \quad \dots \quad \dots \quad (2)$$

Both calculations should be in substantial agreement with one another.

Report as less than 1% for values less than 1%.
Report to the nearest 0.5% for values of 1 to 9%.
Report to the nearest 1% for values above 9%.

NOTES

- 1 Flasks which have been in much use should be avoided since these can be readily perforated by attack from the caustic solution.
- 2 A separating funnel with a large bore tap is desirable to minimise possible blockage by flocculent matter (see 5.8).
- 3 It may not be possible to completely separate with the aqueous layer insoluble matter formed at the interface of the two liquid phases, but it is important to remove all traces of insoluble matter from the ether extract before proceeding to 5.12.

APPENDIX E

Filtration Technique for MQPI Group I Samples Exhibiting Abnormal Appearance After Removal of VCC

1. Introduction

The sample for filtration will comprise, in accordance with the scheme for examination of MQPI Group I samples, the residue obtained from application of STM No. 1 to the original sample.

The present procedure determines whether or not the abnormal appearance of the sample would be eliminated by the filtration step of the Dalton reclamation technology.

2. Apparatus and Materials

- 2.1 500 ml. Buchner flask connected to a suction pump or vacuum line, and fitted with a porcelain Buchner funnel 80 mm i/d.
- 2.2 Two 250 ml. measuring cylinders.
- 2.3 Glass pouring rod.
- 2.4 Flat-bottom tamping rod or glass vessel having a flat bottom of approximately 30 mm diameter.
- 2.5 70 mm Whatman No. 541 filter paper.
- 2.6 Filter aid comprising "Hyflo Supercel" obtainable from Johns Manville (GB) Limited, Ryde House, 391 Richmond Road, Twickenham, Middlesex TW1 2EQ. (Telephone: 01-891-0813).

3. Procedure

- 3.1 Prepare a filter bed by placing the filter paper in the Buchner funnel, and distributing uniformly over the upper surface of the paper 10 g. of the filter aid. Carefully tamp down the filter aid to ensure adequate packing over the whole of the filter area.
- 3.2 Filter through the filter bed 200 ml. sample at ambient laboratory temperature, and suction of approximately 600 Torr. (Note 1).
- 3.3 Transfer approximately 70 ml. of the filtrate to a 250 ml. measuring cylinder, and inspect its appearance diametrically in transmitted and reflected daylight. (Note 2).

4. Reporting

Report the appearance of the filtrate as "abnormal" or "normal" according to which is relevant when the filtrate is compared under the same conditions with the normal appearances of uncontaminated used MIL-L-7808 turbine engine lubricants.

Notes

1. Thoroughly agitate the sample immediately before measuring out the 200 ml. aliquot, and each time any part of the latter is transferred to the filter bed, so as to ensure distribution throughout the sample of any particulate matter which may have settled out.
2. Ignore traces of filter aid which may have passed through the filter paper. Should this be excessive, pass the filtrate through the used filter bed, and repeat the procedure under 3.3.

APPENDIX F

HPLC Methodology Employed for Determination of Inhibitors

1. Equipment

The equipment comprised an Applied Chromatography pump and UV Monitor, a Hamilton Instruments Chart Recorder and LDC Integrater. Columns used were 250 mm x 5 mm with zero dead volume fittings.

2. Test Conditions

Column	Spherisorb ODS 10 μ m
Mobile Phase	10% water in Acetonitrile v/v
Detection	UV @ 254 nm
Flow Rate	2 ml/minute

3. Standardisation

The equipment was firstly standardised by means of nine primary standards, each containing a different inhibitor and was thereafter frequently checked for performance by running through, between analyses of the lubricant samples, a secondary standard containing three of the inhibitors.

3.1 Primary Standards

The primary standards were prepared from a commercial tetra-ester base stock, Herculube J, and each of the following inhibitors:-

4,4' - Dioctyldiphenylamine
Phenyl-1-Napthylamine
N-(4-Octylphenyl)-Napthylamine
3,7 - Dioctylphenothiazine
N-Allyl-3, 7-Dioctylphenothiazine
N-Benzyl-3, 7-Dioctylphenothiazine
Phenothiazine
Benzotriazole
Anthranilamide (2-Aminobenzamide)

About 1.0000 g of inhibitor was dissolved in the base stock to produce about 100.0000 g of each standard.

Standardisation was carried out by dissolving 1.0 g of the standard in 50.0 g of the Mobile Phase and then injecting 10 μ l of this solution on the column by means of a Rheodyne valve and 10 μ l loop.

3.2 Secondary Standard

The secondary standard was prepared by dissolving the following inhibitors in the tetra-ester base stock:-

PAN	0.4033% w/w
MOPAN	0.7922% w/w
DODP	1.1554% w/w

The performance checks were carried out as described above for standardisation under 3.1.

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