

**THE DEGRADATION AND ANALYSIS OF LUBRICATING OIL  
IN DIESEL ENGINES.**

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## ABSTRACT

Investigations into lubricating oil degradation and engine wear were carried out during the course of this work. Lubricating oil degradation models were studied and verified. This study has resulted in the development of an integrated, miniaturised, automated oil analysis system for the determination of water content, Total Base Number and Total Insoluble Matter for new and used oils.

The study on the engine wear and oil degradation was based on two air-cooled Petter AA1, single cylinder engines running on a 1% sulphur diesel fuel and a minimum military specification oil (OMD 75). The results obtained indicated that the combination of engine operating conditions, diesel fuel and lubricating oil used, resulted in the premature loss of oil consumption control due to severe bore polish which was caused by corrosive wear. Oil analysis methods were developed requiring minimal quantities of oil sample in order not to disturb the engine/lubricating oil system integrity. The oil analysis methods developed were automated into a single integrated instrument for the determination of water content, Total Base Number and Total Insoluble Matter for new and used oils using 1 gram (or less) of oil sample and with analysis times in the region of three minutes for doing all three analysis.

A detailed study into new and used formulated oil chemistry revealed that the measurement of Total Base Number as determined by the Institute of Petroleum standard test methods (IP 177 and IP 276) provided information that were over-estimates of the true levels of basicity of the oil. A new technique, based on the same chemistry as the original (IP) method, was developed for the Total Base Number determination with improved end-point detection for not only new oils, but more importantly for used oils as well. Other oil analysis data obtained during this study revealed the need to modernise the existing Industry test methods with regard to chemistry, equipment and functionality, for example Total Acid Number determination.

The data obtained from the analysis of the used oil was studied and the rates of change of each of the measured parameters were calculated, based on the Quasi-Continuous Stirred Tank Reactor model. The data obtained from this model was compared to two previously proposed models which indicated that the QCSTR model is a better model for representing the degradation of lubricating oils in running engines.

This work has shown the need for the trapping of oil from the top-ring zone to understand the nature of the degradation and interaction of this oil with that (bulk) oil in the sump in order to successfully model the degradation characteristics of the oil.

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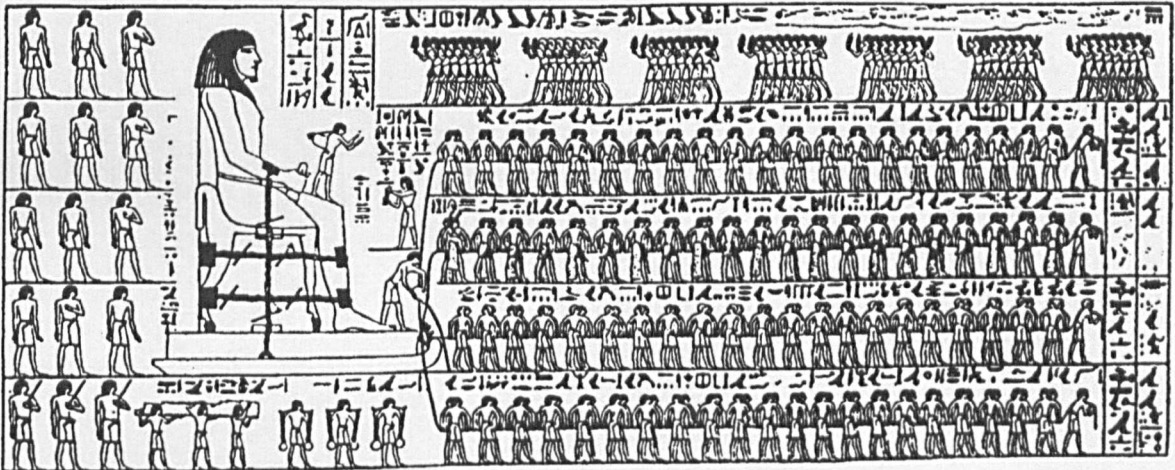
# CHAPTER 1.

## 1. INTRODUCTION.

### 1.1 History of Friction, Wear and Lubrication.

The record of the birth of lubrication is lost in antiquity. Ever since man has tried to drag loads over the ground he has been aware of the existence of friction. Although he could not explain friction, he knew how to reduce it. For example, a mural painting in a grotto at El Bersheh (*c 1900 B.C.*) shows a colossus being pulled along on a sledge while a man standing at the front of the sledge pours a lubricating oil in its path, Figure 1. An Egyptian chariot found in a tomb (*c 1400 B.C.*) had axle grease.

**FIGURE 1:** PART OF A MURAL PAINTING SHOWING A MAN POURING LUBRICATING OIL IN THE PATH OF A COLOSSUS BEING DRAGGED BY SLAVES. Source: [1].



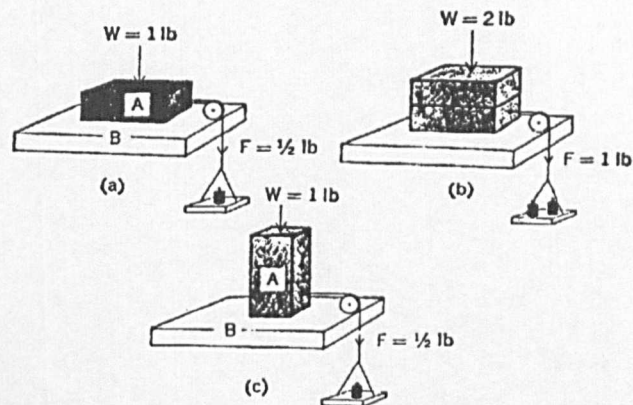
No scientific advance was achieved in the understanding of lubrication or friction field for almost 3000 years. In the middle of the fifteenth century Leonardo da Vinci [2] deduced the two basic laws of friction two hundred years before Newton [3] clearly defined them. Leonardo da Vinci wrote the first law of friction as “friction produces double the amount of effort if the weight be doubled”, that is, the friction,  $F$ , is proportional to the load,  $W$ . He also observed that the area of the surfaces in contact had little effect on the friction; this is the second law of friction.

$$F = \text{constant} \times W \quad \text{Eqn. 1}$$

The constant is the coefficient of friction, usually written  $\mu$ . The coefficient of friction depends on the nature of the materials which are in contact. The coefficient of friction between two bodies is not constant but varies with change in load and sliding speed ,

Figure 2. The static friction, which is the force needed to start one body moving over another, is always greater than the dynamic friction, which is the force needed to keep the first body moving at the same speed once relative movement has started.

**FIGURE 2:** A SIMPLE METHOD FOR MEASURING FRICTION BETWEEN BODY 'A' RESTING ON SURFACE 'B'. Source: [1].



There were two developments in the seventeenth and eighteenth centuries which had a profound effect on the progress of science and technology. One was the establishment of the numerous Academies of Science in Europe and America, such as the Royal Society of London founded in 1662. The second factor was the growth of mechanically driven machinery during the Industrial Revolution. Until that time primary power had been provided by men, horses, windmills and crude water mills. The first steam engine using a piston in a cylinder was constructed by Denis Papin (1647- 1712) in France. Guillaume Amontons [4] published a paper in 1699 in which he rediscovered the two laws of friction originally derived by Leonardo da Vinci. Thomas Newcomen developed the first practical steam engine in 1705 which was used for pumping water from English mines. Captain Nicholas Cugnot built the first self-propelled road vehicle in 1770 with a top speed of 3 m.p.h. for pulling guns.

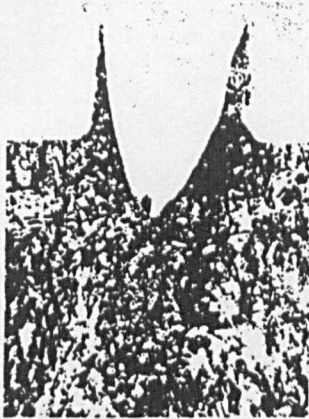
The friction between two dry surfaces arises from two main sources, adhesion and deformation, and the most important is adhesion. Amontons thought that friction arose from the work done in lifting one surface over the roughness on the other. John Theophilus Desaguliers [5], however, pointed out that polished surfaces adhere and thus increase friction. Charles Augustin Coulomb [6] favoured the roughness theory of friction and devised experiments to back-up his point of view. It is difficult to imagine, for example, that two smooth pieces of cast iron can stick together in the same way as adhesive tape, but in fact all materials will stick together to some extent.

The smoothest engineering surfaces are rough when viewed under a high-powered



microscope, Figure 3. Two solid surfaces touching one another will in fact only be in contact at the peaks of their asperities. The asperities are very small peaks on the solid surface, of the order of  $10^{-6}$  mm<sup>2</sup> in area. If two surfaces touch, even with a load of a few grammes, the load will be carried entirely on a small number of these asperities, and the actual contact pressures may be as high as 200 000 psi (1 400 MN/m<sup>2</sup>). Such enormous pressures can deform the asperities on hardened steel or cast iron surfaces and even make them weld together.

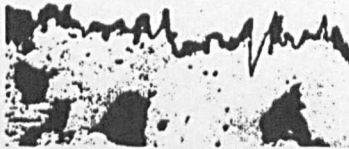
**FIGURE 3:** MICROSCOPIC SURFACE STRUCTURES. Source: [1].



(a) Oblique section of pin scratch in copper showing raised edge and deformation below the surface. Vertical magnification 2,000 times.



(b) Finely turned copper surface. Surface roughnesses are about 200 microinches. Vertical magnification 2,000 times.



(c) Finely abraded steel surface. Irregularities about 20 microinches. Vertical magnification 1,200.



(d) Finely polished steel surface. Irregularities about 4 microinches. Vertical magnification 1,200.

The other main component of friction, deformation friction, is usually small. Nearly 150 years passed from the time of Coulomb before it was realised that friction was due to work done in deforming individual asperities according to the laws of elastic (temporary) and plastic (permanent) deformation. If it is elastic, then the energy which is used to produce deformation will be recovered when the surface returns to its original shape and there will be no net friction. If it is plastic, then there will be a permanent change in shape, resulting in a small amount of deformation friction. There is one complication in that when some substances deform elastically, there is a delay, or “hysteresis”, in their return to their original shape. When this happens, the energy released may be too late to be returned to the sliding system, and there will then be a net frictional loss. This can be important for certain plastics, especially

certain rubbers. "High hysteresis" rubbers for vehicle tyres are deliberately formulated to produce high hysteresis friction. In addition, elastic deformation can cause some loss of energy in the form of heat, and can contribute to fatigue damage.

It has long been known that liquids and greases reduce the friction between sliding surfaces. Until beyond the middle of the nineteenth century it was believed that the liquid or grease filled the surface hollows and so presented a smoother surface for sliding. This point of view was shared by Amontons, Coulomb and engineers of that time. Until the Industrial Revolution animal and vegetable oils were the lubricants in general use. In fact it was only in the latter half of the last century that their limitations were becoming apparent. The introduction of the reciprocating engine, particularly the heavy duty internal combustion engine, gave rise to a demand for cylinder lubricants which would not lose their physical and chemical properties at high temperatures. This demand, coupled with the rapidly increasing demand for animal and vegetable oils for other purposes, resulted in an increase in their cost which led to the wide adoption of mineral oils for lubrication purposes. Animal and vegetable oils, however, still play an important role in the manufacture of compounded oils and greases today. The physical properties of fatty oils are relatively constant but those of mineral derivatives can vary considerably, for example viscosity.

It is not clear at what stage mineral oils were first used as lubricants. It was probably a case of a product being generally available and its particular application being accidental. Petroleum was long used for medicinal and illuminating purposes and was available from seepages from the earth as surface deposits. The earliest well drilled for the specific purpose of obtaining oil is credited to 'Colonel' Drake of the Seneca Oil Company. This well was drilled in 1859 in Titusville, Pennsylvania and had a depth of 69 feet. The modern petroleum industry is generally regarded as starting from this date.

As late as 1890, Phillips [7] in his 'Engineering Chemistry' gives the following list of lubricants and the best purposes for which they could be applied (Table 1).

He adds the note:

'It may be stated, however, that in all cases where possible, a mineral oil of suitable body should be used, especially for cylinders, the high temperature of which decomposes fatty oils with the production of free fatty acids which attack copper, iron, etc., forming metallic soaps which cause much damage to fittings, etc.'

**TABLE 1:** AN EARLY LUBRICANT APPLICATION LIST. Source: [7].

For steam cylinders	Heavy mineral oils, lard, tallow rape oil, etc.
Ordinary machinery	Rape oil, lard oil, tallow oil, and medium mineral oils
For great pressures with slow speed	Tallow, lard oil, palm oil, grease, etc.
For heavy pressures and high speeds	Sperm oil, rape oil, castor oil, medium mineral oils
For light pressures and high speeds	Sperm, refined petroleum, olive, cottonseed, rape and mineral oils
Watches, clocks, etc.	Olive, porpoise, neatsfoot, light mineral and clarified sperm oils

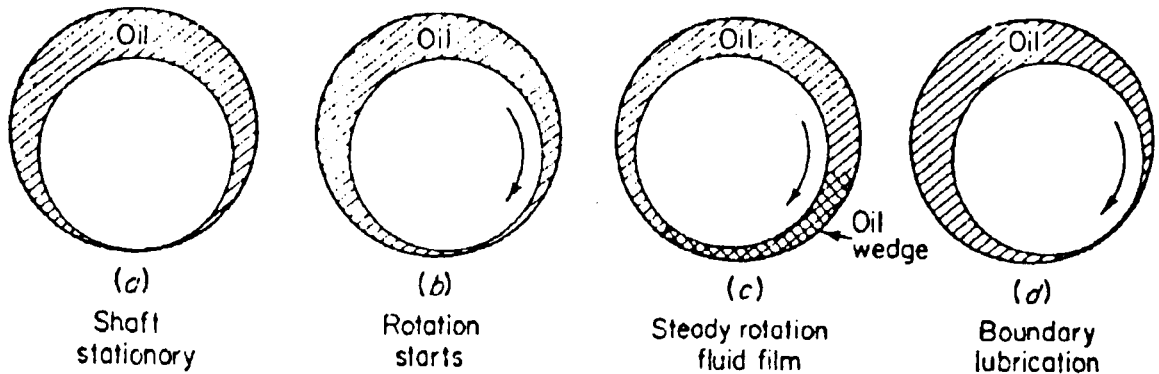
The invention of the steam engine and the consequent use of bearing surfaces in rapid relative motion stimulated much improved techniques of lubrication. The bearing surfaces were no longer in occasional contact, as in boundary lubrication, but were separated by a fluid film thick enough to prevent any contact at all. The word hydrodynamic conveys two ideas: a liquid (hydro) and motion (dynamic). Hydrodynamic lubrication simply means lubrication which is achieved by movement of a viscous liquid between surfaces whose geometry produces a convergent wedge of liquid.

The modern period of lubrication theory starts with the classical work of Osborne Reynolds [8] on the behaviour of shafts or journals in bearings. His theoretical analysis was based on the elegant experimental studies by Beauchamp Tower [9], who was concerned with the behaviour of axles and bearings in locomotive engines.

Tower had found that when the system was running effectively a high hydrostatic pressure was set up in the lubricant film. A paraphrase of Reynolds' explanation, published in 1886, follows: "If a shaft or journal rotates in a clockwise direction in a dry bearing it crawls up the right-hand side of the bearing as shown in Figure (4). If, however, the bearing contains oil and the system runs properly the shaft is displaced to the left side of the bearing and drags a converging wedge of oil between it and the bearing surface. As a result, there is an increase in velocity of flow as the lubricant passes through the narrowing constriction between the moving surfaces."



**FIGURE 4:** LOADED SHAFT IN A LUBRICATED BEARING. Source: [10].



Reynolds showed that because the oil is viscous it produces a pressure build-up in the oil wedge which under favourable conditions is sufficient to keep the surfaces apart. When fluid film or hydrodynamic lubrication prevails, the oil film separating the journal from the bearing surface is of such thickness as to ensure that the asperities of each of the surfaces are kept well apart and that motion takes place by the shearing of successive layers of the lubricant. The coefficient of friction in a given bearing is dependent upon the viscosity of the lubricant. The distance of nearest approach decreases with increasing load and lower shaft speeds.

Reynolds' contribution to lubrication theory was to identify the important parameters and make a number of assumptions as follows:

1. Laminar flow of lubricant within the bearing clearance.
2. Constant viscosity; the temperature rise due to shearing of the oil and the effect of pressure on viscosity are neglected.
3. Superficial dimensions of the oil film are much greater than the film thickness, so that pressure can be assumed to be constant with respect to depth.
4. Pressure is constant along any plane in the oil film perpendicular to the direction of sliding.
5. All oil entering the in-flow edge of the bearing leaves by the out-flow edge; there is no 'side leakage'.

Reynolds' work has stood the test of time well. It is now understood how the liquid film generates a pressure between moving surfaces. This pressure can be calculated to determine how viscous the oil should be and how close the clearance between shaft and bearing should be, if the oil film is to be able to keep the surfaces apart. Reynolds showed that if a slider bearing has infinite length in the z-direction, that is, in the plane

of the oil film perpendicular to the direction of sliding, the pressure distribution within the oil film can be expressed in the one dimensional form:

$$\left(\frac{d}{dx}\right) h^3 \frac{dp}{dx} = 6\eta U \frac{dh}{dx} \quad \text{Eqn. 2}$$

The above equation connects the normal pressures,  $p$ , acting on the bearing surfaces with the velocity,  $U$ , of the moving surface, the viscosity,  $\eta$ , of the oil and the film thickness,  $h$ , at any point.

A special type of hydrodynamic lubrication can take place in certain heavily loaded contacts such as in ball or roller bearings and many types of gear. If the geometry and the type of movement are suitable, lubricant can be trapped in the entry zone of such a contact, and become subject to very high pressures as it is squeezed into the confined space in the most highly loaded part of the contact. These pressures have two important effects. They cause the viscosity of the lubricant to increase considerably, thus increasing its load carrying capacity. At the same time they cause the loaded surfaces to deform elastically in such a way as to spread the load over a greater area. This phenomenon is known as elasto-hydrodynamic lubrication as it is controlled by elastic and hydrodynamic effects. Several equations have been produced to calculate the elasto-hydrodynamic lubrication film thickness; probably the best known is the Dowson-Higginson Equation [11]:

$$h = \frac{2.65 (\eta_0 U)^{0.7} R^{0.43} \alpha^{0.54}}{E^{0.3} \zeta^{0.13}} \quad \text{Eqn. 3}$$

where  $\zeta$ , is the contact pressure;  $R$ , the effective radius;  $E$ , Young's modulus of elasticity;  $\eta$ , is the viscosity of the lubricant in the entry zone; and  $\alpha$ , the extent to which viscosity increases with pressure.

Although, technically, hydrodynamic lubrication refers to lubrication by a liquid, it can also be applied to lubrication by gas, provided that the load and speed conditions are suitable for the very low viscosity of gases.

The significance of boundary lubrication conditions had not been appreciated until the first systematic investigations into the mechanism of thin-film lubrication were carried out by Hardy [12] who first used the term 'boundary' lubrication. Under boundary lubrication the distance apart of the mating surfaces is very much less than for hydrodynamic lubrication conditions, being of the order of the height of the surface

asperities. When the oil film is squeezed out, metal-to-metal contact can take place and the load would be carried on the high spots of the journal and the bearing. Appreciable heat would be generated and the two surfaces may become welded together. When the two surfaces adhere together, 'seizure' is said to take place. If motion is then forced, removal of metal may take place from one or both the surfaces resulting in what is known as 'scuffing'. In practice, seizure or scuffing, is delayed by the fact that metals tend to have oxide films on their surfaces and these temporarily prevent direct metal-to-metal contact. In addition to the surface oxide layers, adsorption of lubricant or other chemicals may become attached to the metal surface.

## 1.2 Engine Lubrication Systems.

The simplest method of applying lubricant to a bearing is from an oil-can through a small hole in the top of a bearing. This method is crude as it allows moisture and solid contaminants into the bearing. A simple improvement is to close the hole by a spring-loaded ball which fulfils the requirements of a lubricator by excluding dirt and moisture. In addition, a lubricator should have adequate storage capacity to minimise constant attention. The simplest possible lubrication system consists of a gravity feed of the lubricant to the point of application. The gravity supply tank must have the necessary head for oil flow to take place. The tank may be replaced by a pump in a 'forced- feed system'. The oil is either consumed or lost, that is, the system is a 'total loss' one.

In many cases, for example in enclosed engines it is possible, after the oil has done its work, for the oil to flow into a sump from where it can be recirculated. In a total loss system fresh oil has to be continuously fed into the system. In a recirculation system the same oil is used continuously although some oil loss may occur in leakages, combustion, evaporation and degradation which then requires the oil to be changed regularly or the level 'made-up' with fresh oil. In a recirculation system any particulate matter must be removed by filtration whereas in a total loss system any dirt would be washed away with the oil.

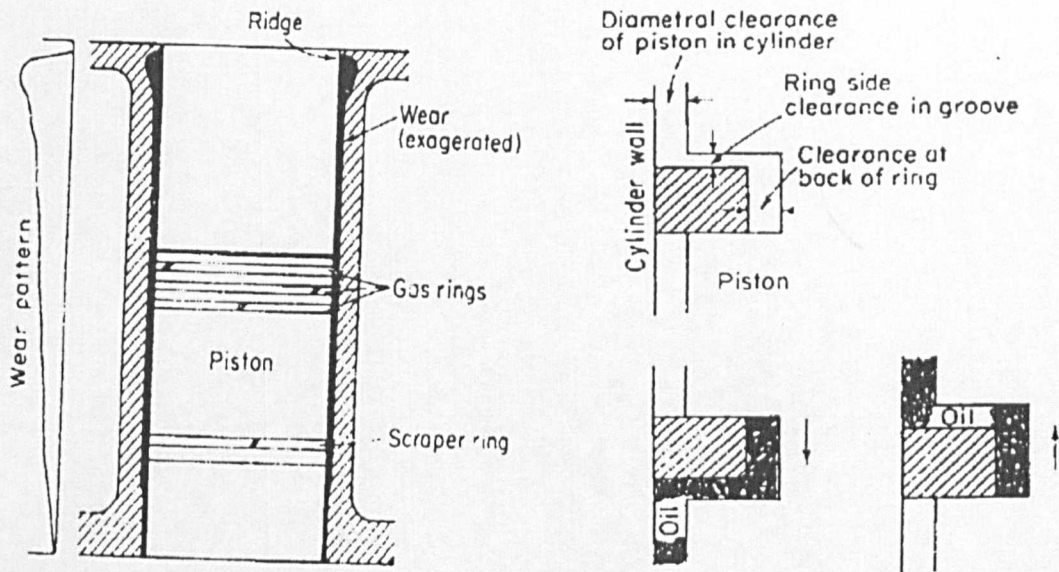
In enclosed reciprocating engines it was common practice to place the sump at the bottom of the crankcase so that as the crankshaft revolves, the big-end connecting-rod bearings dip in the oil and are thus regularly lubricated. At the same time oil is splashed on to the walls of the cylinders and the small-end bearings of the connecting-rod. A constant mist of oil exists in the crankcase whilst the engine is running. This method of lubrication is known as 'splash lubrication' and it requires that the oil in the sump to be maintained above some definite, minimum level. Small internal combustion engines, up to 250 cc, still use this.

In the high-speed totally enclosed steam reciprocating engine, it was inevitable that steam would mix with the oil in the crankcase. High working temperatures and the churning together of oil, air and water leads to the oxidation of the oil, the formation of water-oil emulsions and the deposition of sludge in the crankcase. Large steam turbines are invariably fitted with forced-feed recirculation systems where the lubricant may also have to function as the operating fluid in governors and control gear. The high speed of a marine turbine is reduced to low propeller speed using double helical gearing. Efficient lubrication of the gear teeth is called for and the oil has to act as a coolant.

Small two-stroke internal combustion engines may operate on a 'total loss' system. Early systems involved injecting or supplying a continuous drip feed of oil to the crankcase, but the modern method is to dissolve the lubricating oil in the petrol. The oil is deposited in the crankcase when the fuel charge is compressed. The most common system, universal in automobile engines, is the wet sump system. Splash is relied upon to lubricate the cylinder walls, the big end and the small end bearings. A gear or valve type pump is generally used to force oil to the crankshaft, rocker gear, etc., the surplus oil draining back to the sump. In the dry sump system a separate oil tank is used and the amount of oil in the sump is reduced to a minimum. Oil from the tank is pumped to the connecting rod bearings, the camshaft and crank bearings. Lubrication of the cylinder walls and also cooling of the underside of the piston may be effected by an oil-jet in one of the crankwebs. The oil then drains back to the sump from which it is drawn through a filter back to the tank by means of a 'scavenge' pump. The scavenge pump usually has a greater capacity than the circulating pump to ensure that there is no accumulation of oil in the crankcase. The advantages of this system are that better filtering and cooling of the lubricating oil is possible. The system can be used in radial, inverted engines and also in any type of aircraft reciprocating engine where inverted flight is possible.

The disadvantage of wet and dry sump engine lubrication systems is that the oil is expected to cope with both extremes. The same oil is used for cylinder lubrication where it is subjected to high temperatures and for piston cooling and bearing lubrication, in which capacity it must be a heavy duty lubricant. It is also used for the lubrication of camshafts and timing gears, and in some cases as a hydraulic medium for operating accessories. An improvement on this would be to have separate lubrication systems for bearings and cylinders as in the case with very large marine diesel engines. The oil may be supplied under pressure to a number of points in the cylinder through 'quills' each of which is supplied by a pump. The spring-loaded valve in the quill prevents blow-back of the combustion gases into the oil feed lines.

**FIGURE 5:** Source: [10] (a) CYLINDER BORE WEAR. (b) PISTON-RING PUMPING.



In a total loss system, oil consumption is within the control of the user, but it is necessary to ensure that the oil consumption is adequate. This applies to small two-stroke petrol engines as well as to very large marine diesel and steam engines in which there are separate feeds to the cylinders. In other internal combustion engines cylinder lubrication is by means of a splash or crank-web oil jet. For a given size of engine, the amount of oil distributed over the cylinder walls will depend on the stroke/bore ratio, the engine speed, and the scraping action of the piston rings. The net scraping action of the piston rings results in the removal of the excess oil from the cylinder walls and its return to the sump. Oil passing upwards past the piston will enter the combustion chamber and ultimately be consumed. This is the principal source of loss in the engine circulatory systems. As wear takes place, clearances increase and, generally, greater loss of oil results. This is particularly so in the case of internal combustion engine cylinders.

Wear takes place on the cylinder wall, around the circumference of the piston, in the piston ring grooves and on the sides and faces of the piston rings. Figure 5(a), shows the cylinder wear grossly exaggerated. A ridge is formed at the top of the piston ring travel and when new rings are fitted this ridge should be removed. The diameter of the piston is reduced by wear and as a result of this, and cylinder wear, the clearance between piston and cylinder is increased and a greater volume of oil is carried into the combustion chamber. A temporary reduction on the increased oil consumption can be made by using an oil of greater viscosity, but this has its obvious disadvantages.

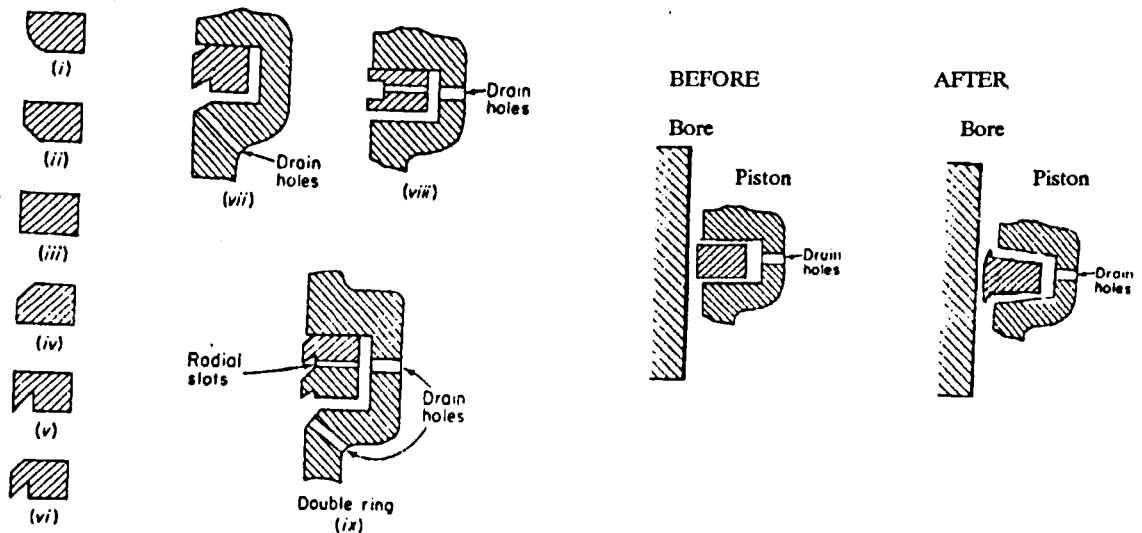
A result of piston ring groove wear combined with wear on the side faces of the rings is that piston rings tend to act as pumps, pumping oil up into the combustion space and thus increasing oil consumption. On the downward motion of the piston the ring is in contact with the top of the groove and the space beneath it becomes filled with oil. On the up-stroke this oil is transferred from beneath the ring, past the back of the ring, into the space above the ring and ultimately into the combustion chamber, Figure 5(b). Various special types of piston rings have been devised to overcome this defect and thus reduce oil consumption, and to prolong the engine life. The best remedy for excessive oil consumption is a cylinder re-bore and fitting new pistons and rings. Piston rings may also wear on their rubbing faces and may lose their "springiness" resulting in reduced ring wall pressure. Top rings are particularly subject to heavy scuffing due to the onerous lubrication conditions at the top of the stroke and the intrusion of small pieces of hard carbon dislodged from the piston crown or the combustion chamber.

Control of oil consumption in an internal combustion engine results from the combined scraping action of all the rings, but most of this work is done by the bottom rings which are known as scraper rings. The top piston rings act as gas seals. Various designs of scraper rings in cross-section are shown in Figure 6(a), the severity of the individual scraping action increasing from top to bottom. The scraping action is least with a rounded edge and greatest with an acute angled 'cutting' edge; the action may be increased by providing each ring with two scraping edges and suitable oil escape holes in the rings and piston ring grooves. The maximum scraping action will not be obtained if suitable escape holes for the scraped-off oil are not provided or if these holes are not kept open. The scraping action of any ring will also depend upon the circumferential wall pressure it exerts upon the cylinder wall. Various methods have been devised for assessing the value of, or the variation in, circumferential ring-cylinder wall pressure but none has come into general use. Piston compression rings can be obtained with one degree of face taper intended to facilitate running in. The amount of initial narrow land removed after a short duration run permits an assessment of the circumferential distribution of piston ring wear.

The distribution of wear can be studied from wear patterns, for example, cylinder wear and piston ring groove wear patterns can be obtained from direct measurements using a micrometer or feeler gauges. Wear patterns can serve to indicate the nature of relative motion of the parts concerned, for example, the piston ring groove wear pattern, Figure 6(b), could be explained on the basis of ring rotation plus the rocking of the piston at the end of the stroke. Wear traces on the upper faces of rings may indicate ring "flutter". The amount of piston-ring and bearing wear can be found from changes in their mass before and after tests of known duration. Assessment of overall

wear can be made from the metallic content of the ash of used oils. Radioactive tracers can be used to measure wear in individual parts by determining the increase in radioactivity of the sump oil.

**FIGURE 6:** Source: [10]) (a) PISTON RING DESIGNS. (b) PISTON RING GROOVE WEAR.



Wear will be apparent after two surfaces have been rubbing together for a considerable period. It is a point of good design that the maximum amount of wear is confined to those parts that can be readily replaced, as an example, journals which cannot be readily replaced are made of hard materials, while mating bearing 'brasses' are made of soft material so that most of the wear takes place in the softer bearing material. When this type of wear takes place the material appears to have been removed by a process analogous to machining. As a consequence, it is referred to as cutting wear and results from actual mechanical removal of metal. If good fluid film lubrication could always be maintained, that is, if the mating surfaces were always separated by a film of lubricant, little, if any, cutting wear would result, and this would only take place during starting and stopping when full fluid film lubrication is not possible.

Abrasive wear results from the intrusion of some abrasive such as grit, which can be reduced to a minimum by the use of air and oil filters. Wear due to scuffing can be reduced by improved lubrication and by the use of extreme pressure additives which form tough, adherent films on the mating surfaces. Corrosive wear results from chemical action of acidic degradation products of the oil, residual acids in the oil or from combustion gases (e.g. from sulphuric acid to weak organic acids) on steel and

bearing metals such as copper, bronze, tin and aluminium. The corrosive wear is accelerated by the presence of water in the oil and high temperature.

A lubricant has two functions: the reduction of friction and the elimination of damage to the sliding surfaces. Work lost due to friction is minimised by reducing the friction which also reduces the associated frictional heat produced. In addition, lubricants are usually expected to reduce wear, act as a coolant to prevent overheating and to prevent corrosion. The two main factors affecting the choice of lubricant are usually the speed and the load. To simplify the problem of choosing between the available lubricants, it is convenient to divide them into four basic types. These are:

1. Oils - A general term used to cover all liquid lubricants, whether they are mineral oils, natural oils, synthetics or emulsions.
2. Greases - Technically these are oils which contain a thickening agent to make them semi-solid, but it is convenient to include anti-sieze pastes and semi-fluid greases under this heading.
3. Dry lubricants - These include any lubricant used in solid form, and may be bulk solids, paint-like coatings or powders.
4. Gases - The gas usually used in gas bearings is air, but any non-reactive gas may be used.

The broad properties of these four types of lubricants are summarised in the Table (2) below.

The advantages and disadvantages of oils stem from their ability to flow easily. Thus, on their credit side it is very easy to pour them from a container, to feed them into a bearing by dripping, splashing or pumping, and to drain them out of a machine when no longer fit for use. Most important of all, with proper design the bearing itself can be made to feed oil into the loaded zone. Other advantages are cooling of the bearing by carrying away heat and cleaning it by removing debris. On the debit side, oil can equally easily run away from a bearing, leak out of a container or machine, migrate away over the surrounding surfaces, and even evaporate if the bearing is hot and well ventilated. In addition, because it is a liquid it does not form an effective seal against dirt or moisture from getting into the bearing.



**TABLE 2: PROPERTIES OF BASIC LUBRICANT TYPES.** Source [13].

Lubricant property	Oil	Grease	Dry lubricant	Gas
1. Hydrodynamic lubrication	Excellent	Fair	Nil	Good
2. Boundary lubrication	Poor to excellent	Good to excellent	Good to excellent	Usually poor
3. Cooling	Very good	Poor	Nil	Fair
4. Low friction	Fair to good	Fair	Poor	Excellent
5. Ease of feed to bearing	Good	Fair	Poor	Good
6. Ability to remain in bearing	Poor	Good	Very good	Very good
7. Ability to seal out contaminant	Poor	Very good	Fair to good	Very poor
8. Protection against atmospheric corrosion	Fair to excellent	Good to excellent	Poor to fair	Poor
9. Temperature range	Fair to excellent	Good	Very good	Excellent
10. Volatility	Very high to low	Generally low	Low	Very high
11. Flammability	Very high to very low	Generally low	Generally low	Depends on gas
12. Compatibility	Very bad to fair	Fair	Excellent	Generally good
13. Cost of lubricant	Low to high	Fairly high	Fairly high	Generally very low
14. Complexity of bearing design	Fairly low	Fairly low	Low to high	Very high
15. Life determined by	Deterioration and contamination	Deterioration	Wear	Ability to maintain gas supply

Greases behave in many ways as oils do, but are used where the advantages of easy flow are outweighed by the disadvantages. Greases do not easily leak out of a machine or container, or migrate away, and form an effective seal against contaminants. On the other hand, greases are much less easy to feed into a bearing, and are almost useless for cooling. Solid lubricants are rather like the extremes for greases, where the lubricant will not flow at all and similarly gas lubricants are like the extremes of oils, where the flow properties are almost too good. Solid and gas lubricants have very specialised advantages and disadvantages and are generally used only in special situations.

A lubrication system should never be made more complex than it needs to be in order to work properly. The simplest possible technique will often be the most reliable as well as the cheapest. One of the best ways to select a lubricant, and a lubrication system, will therefore, be to start with the simplest possible arrangement and only to alter it where it is necessary to overcome problems. A general indication of the way in which different components need different lubricant properties is given in the Table (3) below.

**TABLE 3.** LUBRICATION REQUIREMENTS OF DIFFERENT COMPONENTS. Source [13].

Lubricant property	Type of bearing				
	Plain journal bearing	Rolling bearing	Closed gears	Open gears, ropes, chains, etc.	Clock and instrument pivots
1. Boundary lubricating properties	*	*	***	***	**
2. Cooling	**	**	***		
3. Friction	*	*	**		**
4. Ability to remain in bearing	*	**		**	***
5. Ability to seal out contaminants		**		*	
6. Temperature range	**	**	**	*	
7. Protection against corrosion	*	*		**	

### 1.3 The Role of Engine Oil.

For internal combustion engines and compressor cylinders, the oil must give both effective lubrication under very onerous conditions and also act as a high pressure seal that reduces leakage to a minimum between piston, rings, cylinder and valve guides. Since the motion will be reciprocating, it is probable that full fluid film lubrication will not always be maintained. The amount of oil passing the piston into the combustion chamber must be reduced to a minimum so as to keep oil consumption low and, in the case of compressors, to prevent excessive contamination of the compressed gas. An "acceptable" lubricating oil for use in internal combustion engines must have sufficient viscosity at the working temperature of the engine and a high viscosity index so that the oil will not be too viscous when the engine is cold.

For practically all steam engines the steam becomes wet towards the end of the expansion stroke and the water formed tends to wash the oil from the cylinder walls. Bearing in mind the necessity for increased oil adhesion to the mating surfaces, there is a high probability that boundary lubrication conditions will prevail for at least part of the cycle. The emulsions thus formed can be a problem especially in the case of enclosed steam engines, where straight mineral oils are better than compounded oils. In internal combustion engines steam is a product of fuel combustion, and some of the steam may get past the piston rings and condense in the crankcase. In cold weather this water in the crankcase may emulsify with the oil to produce (white) 'cold sludge'. Used oils emulsify more readily than new oils because of oxidation products being present in used oils.

The maximum thermal efficiency,  $\eta$ , obtainable from a petrol engine depends upon the compression ratio,  $r$ ; the higher the compression ratio greater the thermal efficiency, provided that the fuel does not detonate, in a simplified form;

$$\eta_{\text{Otto, Diesel}} = \left(1 - \frac{1}{r}\right)^{\gamma-1} \quad \text{where } \gamma = \frac{c_p}{c_v} = 1.4 \text{ for Air} \quad \text{Eqn. 4}$$

The resistance of a petrol to detonation is expressed in terms of OctaneNumber. Additives such as tetra-ethyl lead are used to increase the resistance of fuel to detonation, that is, it increases the octane rating of the fuel. Within recent years considerable improvements have been made to improve fuels which allowed compression ratios of 9 or 10 being used in gasoline engines. Increased compression ratios and the use of turbochargers, result in increased temperatures at the end of the compression stroke and consequent increased pressure and temperatures throughout

the expansion stroke.

Engine lubricating oils are required to effect lubrication at these increased temperatures and also to act as coolants. During the process of splash lubrication, oil is splashed on to the hot cylinder walls, oil-jets in the crank- webs squirt oil up inside the piston to cool the piston crown and help with cylinder lubrication; at the same time oil flowing through the bearings serves to cool them. If the oil is to function satisfactorily as a lubricant at these elevated temperatures it must have a high viscosity index, see later section. The portion of oil coming into contact with the hot pistons and cylinder walls is liable to 'crack' or decompose into carbon particles, form complex resinous materials or asphaltic products and lighter oil fractions may readily evaporate. The carbon and asphaltic products formed as a result of the oil degradation will work their way into the piston ring grooves where they will tend to "gum" the piston rings. Other decomposition products will appear as a lacquer deposit on the piston skirt and under the piston crown. Some of the oil that manages to pass into the combustion chamber will be burned, or partially burned or turned into carbon together with some of the fuel. This will be deposited on the piston crown, which may require periodic removal (decarbonisation or decoking). In consequence, carbon residue tests are included in oil specifications for use in internal combustion engines.

Other products of oil deterioration are:

1. Fatty acids from the oxidation of aliphatic chains which are likely to attack lead-bronze and cadmium-nickel bearings.
2. Black sludge, a pasty substance which may be deposited in the cold regions of the engine, oil channels or on moving parts. Ideally, it should be held in suspension in the oil until it is removed by the oil filter. Sludge is an oxidation product resulting from the aeration of the hot oil, sometimes referred to as 'hot sludge'.

The lubrication of valve stems and the maintenance of adequate lubrication in the upper portion of the cylinder is a difficult problem. The oil must act as a seal in a narrow, hot, moving surface. In an attempt to ameliorate upper cylinder lubricating conditions, lubricants are sometimes added to the fuel. Such lubricants usually consist of a thin mineral oil with a high ignition point and containing additives such as solvents for asphaltenes, e.g. tetrahydro-naphthalene.

In a diesel engine, temperatures and compression pressures are much higher than in a petrol engine, but the combustion takes place largely at constant pressure and partly at constant volume. In general, the lubrication problems of diesel engines are the same as for petrol engines. Diesel engines are, however larger, and may work on

either the two- or four-stroke cycle. Two-stroke engines suffer from build-up of deposits in their transfer ports, which restrict the flow of incoming air and outgoing exhaust gas, thus impairing its working efficiency.

Piston ring “gumming” may be a serious problem in diesel engines as also may be fuel dilution, products of fuel combustion and sulphur compounds from the fuel. Deposits on the piston skirt usually referred to as ‘varnish’ are present and vary from light brown to black in colour. The nature of the deposits formed in the piston ring zone is important. Paraffinic base oils, which in general have a number of desirable qualities as cylinder oils, such as a good viscosity index and resistance to oxidation, produce hard, fine grained carbonaceous deposits. Naphthenic base oils give a softer type of ‘carbon’. This has led to improvement in other properties of naphthenic base oils by refining methods together with the use of additives, and to the blending of paraffinic and naphthenic base oils.

In large diesel engines having separate lubrication systems for the cylinders and the bearings it is possible to use specially formulated oils containing detergent, dispersant and anti-wear additives for cylinder lubrication. These are different from the sump oil which lubricate the bearings.

A good lubricating oil formulated for automobile engines must, therefore, also keep oil degradation products to a minimum. The degradation products that are formed must be kept in suspension so that they may be removed from circulation by the oil filter.

#### 1.4 Modern Engine Lubricating Oils.

The single most important property of a lubricating oil is its viscosity. As far as actual lubrication is concerned, the only other important factor is the boundary lubrication quality. Many other properties may be important for various applications, but if at any instant the combination of viscosity and boundary lubrication is satisfactory, then the oil has been chosen correctly.

In practice, many other factors must be taken into account, to make sure that the oil continues to lubricate properly over a long period of time and a range of conditions. The following are some of these factors;

1. **Thermal stability.** As an oil becomes hot when used, then it is important that the heat does not induce thermal degradation such that the oil ceases to lubricate properly.

2. **Chemical stability.** The ability of the oil to resist chemical attack by atmospheric oxygen, water, or other substances with which it comes into contact. Chemical stability is related to thermal stability, because the rate of chemical degradation increases with increasing temperature.
3. **Compatibility.** This factor generally refers to the interaction between the oil and other solid materials present as, for example, an oil may cause the rubber seal of a bearing, or shaft, to swell, shrink, soften or harden.
4. **Corrosiveness.** Corrosion arising due to acidic compound production in the oil or environment attacking metal components in the system.
5. **Thermal conductivity.** An important property where the oil is required to conduct heat away from bearings and cylinders. The amount of heat conducted away depends on the rate of oil flow and on the specific heat capacity of the oil.
6. **Flammability.** It is important that the oil should not ignite in use, especially in aviation and coal mining use. Thus, oils must have high flash- points (as defined by ASTM/IP).
7. **Toxicity.** The oil must be safe to use and handle without risks to health or the environment.
8. **Cost and Availability.** The cost of certain synthetic oils may be three times that for a natural formulated oil but the cost must be secondary to its suitability for a particular use. Availability of the correct oil in different parts of the world may become both important and difficult. Long service life of the oil is also desirable.

The word "mineral" originally meant mineral oils obtained from petroleum. The mineral oils used for lubrication were originally just the fractions obtained from the distillation of petroleum which had a suitable viscosity for lubrication, much the same as heavy fuel oils. During the last 50 years the manufacture of lubricating oils has become much more sophisticated. Vacuum distillation allows for enhanced and more efficient production. "Sweetening" is used to remove sulphur compounds. Hydrogenation of unsaturated components produces more stable oils. The chemical constituents of mineral oils are mainly hydrocarbons, which contain mainly carbon and hydrogen. These are of three basic types, the majority of which are paraffins, in which the carbon atoms are in straight or branched chains, but not rings. The second most common type are naphthenes, in which some carbon atoms form aliphatic or alicyclic rings. Finally, there is a small proportion, about 2% of aromatics, in which carbon rings are present, but the proportion of hydrogen to carbon is reduced. There are small quantities of compounds containing oxygen, sulphur, nitrogen and phosphorus, called asphaltenes, present in mineral oils.

Although the amounts of aromatics and asphaltenes are small, they play an important

part in boundary lubrication. If the amount of carbon present in paraffin chains is much higher than the amount in naphthene rings, the oil is called a “paraffinic” oil. If the proportion in naphthene rings is only a little less than the proportion in paraffin chains, the oil is called “naphthenic”. The compositions of typical paraffinic and naphthenic oils are shown in Table 4 below.

**TABLE 4** COMPOSITIONS OF TYPICAL PARAFFINIC AND NAPHTHENIC OILS. Source [13].

Constituents	Percentages present in	
	Paraffinic Oil	Naphthenic Oil
Carbon atoms in paraffin chains	63	52
Carbon atoms in naphthene rings	33	44
Carbon atoms in aromatic rings	2	2
Sulphur (by mass)	0.5	1
Asphaltenes	1	2

### 1.5 OIL VISCOSITY.

When relative motion takes place between adjacent layers of a fluid internal shear stresses arise to oppose the motion. The viscosity of a liquid is its resistance to this motion. Under the same conditions, a liquid with low viscosity will flow more quickly than a liquid of high viscosity. Fluids in which the shear stress,  $s$ , is directly proportional to the rate of shear ( $du/dy$ ), are known as Newtonian fluids, the constant of proportionality being the dynamic viscosity,  $\eta$ :

$$s = \eta \, du/dy \qquad \text{Eqn. 5}$$

Viscosity is measured in several units, and the relationship between the common units is given below. The unit of dynamic viscosity is the Poise and is a quantity such that a force of 1 dyne acting on a surface area of 1 cm<sup>2</sup> will produce shear at the rate of 1 s<sup>-1</sup>, that is;

$$\text{poise} = \text{dyne.s/cm}^2 = \text{g/cm/s}$$

The kinematic viscosity is defined as the dynamic viscosity divided by the density; the unit is the Stoke.

$$\text{Stokes} = \text{poise/g cm}^{-3} = \text{cm}^2 \text{s}^{-1}$$

Table (5) lists other commonly used viscosity units along with the conversion between them. For practical purposes, attempts are being made to concentrate on the unit of "Kinematic Viscosity", the centistoke (cSt) (millimetre<sup>2</sup> per second, mm<sup>2</sup> s<sup>-1</sup>). Water at 20 °C has a Viscosity of 1 cSt, while a 20W/50 oil has a viscosity of about 300 cSt. The temperatures quoted below are those specified in technical procedures, hence they are quoted in non-SI dimensions and units, primarily Imperial units.

**TABLE 5.** VISCOSITY CONVERSION TABLE. Source [14].

This table may be used for approximate conversion from one viscosity scale to another, at the same temperature.

Kinematic centistokes	Saybolt Universal seconds	Redwood No. I seconds	Engler degrees	Kinematic centistokes	Saybolt Universal seconds	Redwood No. I seconds	Engler degrees
3.0	36	33	1.23	50	232	204	6.65
4.0	39	36	1.31	60	279	245	7.92
5.0	42	38	1.40	70	325	285	9.24
6.0	46	41	1.48	80	371	326	10.58
7.0	49	44	1.57	90	419	368	11.9
8.0	52	46	1.66	100	463	406	13.2
9.0	56	49	1.75	110	510	450	14.6
10	59	52	1.84	120	560	490	16.0
11	63	55	1.93	130	610	530	17.3
12	66	58	2.02	140	650	570	18.5
13	70	61	2.12	150	700	620	19.9
14	74	65	2.22	200	940	820	26.8
15	78	68	2.33	250	1160	1010	33
16	81	71	2.44	300	1410	1230	40
17	85	75	2.55	400	1870	1640	53
18	90	78	2.65	500	2320	2040	66
19	94	82	2.76	600	2800	2430	79
20	98	86	2.88	700	3250	2820	93
21	102	90	2.99	800	3700	3250	105
22	107	93	3.11	900	4200	3650	118
23	111	97	3.22	1000	4750	4100	133
24	115	101	3.34	1500	7000	6100	199
25	120	105	3.46	2000	9200	8100	260
30	142	124	4.08	2500	11 600	10 100	325
35	164	144	4.71	3000	14 000	12 300	400
40	187	164	5.35	4000	18 500	16 100	530
45	209	184	5.99	5000	23 000	20 000	660

The most widely used system for classifying oils according to their viscosity is that adopted by the American Society of Automotive Engineers (SAE). This system was devised to replace such vague terms as 'light', 'medium' and 'heavy' as applied to oils. Table (6) below shows the SAE classifications for crankcase, transmission and axle lubricants. It should be noted that an oil will qualify as SAE 10W if it meets either of a pair of specifications, and the same is true of SAE 20W grade. For each of these two grades, the first specification is either based entirely on an acceptable range of viscosity at 0 °F (-17.8 °C) or on an alternative specification of a maximum viscosity at 0 °F in conjunction to a minimum viscosity at 210 °F (98.9 °C). Since these are primarily motor oils, these particular limits are designed to ensure satisfactory winter



starting (hence the suffix W), in addition to maintaining satisfactory lubrication at engine running temperatures.

Hitherto, it was permissible to derive viscosity at 0 °F by extrapolation, having first determined viscosities at 100 °F and 210 °F. However, because of the non-Newtonian characteristics of modern multi-grade lubricating oils, the determined viscosity at 0 °F is almost invariably different from the extrapolated value. In the interests of good cold starting performance, therefore, the major automobile manufacturers consider that the specified 0 °F viscosities of 'W' grades should be measured rather than extrapolated as is currently practised.

**TABLE 6.** SAE CRANKCASE OIL VISCOSITY GRADING. Source [14].

SAE Viscosity Number	Viscosity Units*	Viscosity Range*				SAE Viscosity Number	Viscosity Units*	Viscosity Range*			
		At 0°F		At 210°F				At 0°F		At 210°F	
		Min	Max	Min	Max			Min	Max	Min	Max
5W	Centipoises	—	Less than 1200	—	—	20	Centistokes	—	—	5.7	Less than 9.6
	Centistokes	—	1300	—	—		SUS	—	—	45	58
	SUS	—	6000	—	—						
10W	Centipoises	1200 <sup>d</sup>	Less than 2400	—	—	30	Centistokes	—	—	9.6	Less than 12.9
	Centistokes	1300	2600	—	—		SUS	—	—	58	70
	SUS	6000	12 000	—	—						
20W	Centipoises	2400 <sup>d</sup>	Less than 9600	—	—	40	Centistokes	—	—	12.9	Less than 16.8
	Centistokes	2600	10 500	—	—		SUS	—	—	70	85
	SUS	12 000	48 000	—	—						
	Centipoises	—	—	—	—	50	Centistokes	—	—	16.8	Less than 22.7
	Centistokes	—	—	—	—		SUS	—	—	85	110
	SUS	—	—	—	—						

- The official values in this classification are based upon 210°F viscosities in centistokes (ASTM D 445) and 0°F viscosities in centipoises (ASTM D 2602). Approximate values in other units of viscosity are given for information only. The approximate values at 0°F were calculated using an assumed oil density of 0.9 gm/cm<sup>3</sup> at that temperature.
- The viscosity of all oils included in this classification shall not be less than 3.9 cSt (39 SUS) at 210°F
- Minimum viscosity at 0°F may be waived provided viscosity at 210°F is not below 4.2 cSt (40 SUS).
- Minimum viscosity at 0°F may be waived provided viscosity at 210°F is not below 5.7 cSt (45 SUS).

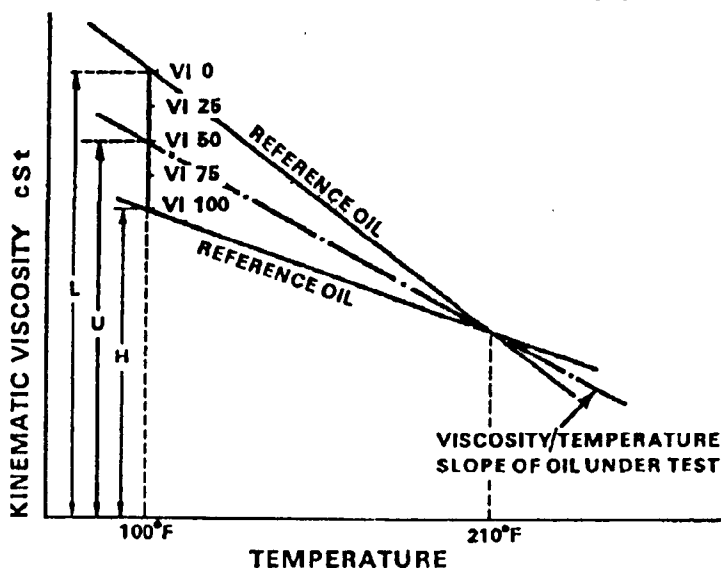
Since the SAE crankcase oil specification is based on viscosity requirements at two temperatures only (0 °F and 210 °F), it becomes possible by suitable formulation to make an oil meeting the requirements of two SAE grades simultaneously. Such an oil is described as a multi-grade oil. For example, a crankcase oil having a viscosity of 1500 cSt at 0 °F (SAE 10W) and 15 cSt at 210 °F (SAE 40) would be classified as an SAE 10W/40 oil. This reduction of viscosity/temperature sensitivity is usually brought about by the addition of viscosity-index improvers, see section 1.6.8 below. The advantage of multi-grade oils is that they allow operation over a considerably wider range of temperatures than would be possible for a single-grade oil.

It must be pointed out that the SAE number is not a rating of oil quality since it covers only viscosity requirements. It does not indicate, for instance, properties such as

detergency and pour-point. Neither does the SAE number in itself give more than an approximation of the viscosity/temperature behaviour of the oil except in the case of 'multi-grade' oils which have low viscosity-temperature variation.

The viscosity of almost all liquids decreases as its temperature increases. It is important to know how much the viscosity changes with a change in temperature. This is best illustrated graphically as shown below, but a much more widely used method is by means of its "Viscosity Index", or VI.

**FIGURE 7.** GRAPH SHOWING METHOD OF CALCULATION OF VI. Source [14].



The viscosity index system was devised by Dean and Davis in 1929 and is widely used in the petroleum industry because of the convenience of the single number it uses to express the viscosity-temperature relationship of an oil. This system is illustrated in Figure 7. The standards chosen for comparison were fractions obtained from a Pennsylvanian oil which was arbitrarily assigned a viscosity index of 100 and a Gulf Coast oil was assigned a viscosity index of zero. These two oils were chosen because, at that time, they represented the absolute maximum and minimum limits of viscosity-temperature sensitivity. The Viscosity Index of an oil is calculated from its own viscosity,  $U$ , at 100 °F (37.8 °C), the viscosity,  $L$ , at 100 °F of an oil of 0 viscosity index having the same viscosity at 210 °F as the sample, and the viscosity,  $H$ , at 100 °F of an oil of 100 viscosity index having the same viscosity at 210 °F as the oil sample (in cSt).

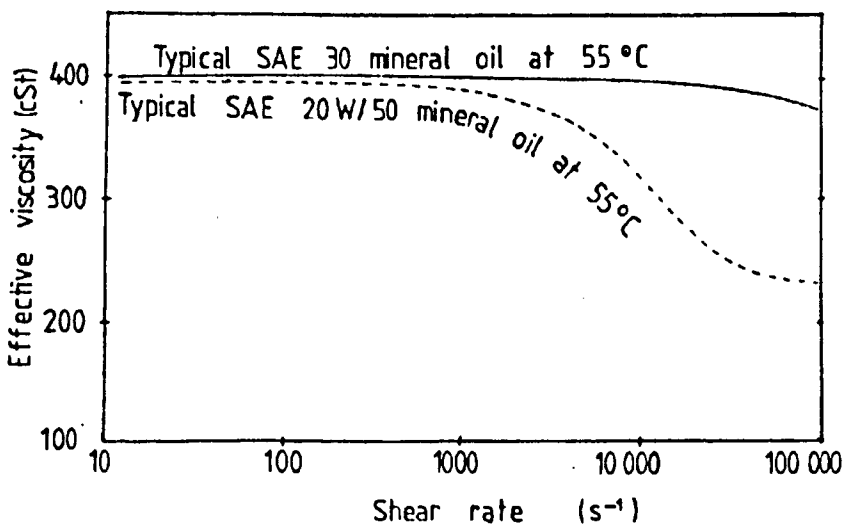
$$VI = \frac{L-U}{L-H} \times 100 \quad \text{Eqn. 6}$$

Substitution in the above equation gives the required VI, where  $L$ ,  $H$  and  $U$  are the viscosities at 100 °F of the zero-VI standard, the 100-VI standard, and the sample respectively. The normal range of VI is from 0 to 100. A VI of 0 indicates a rapid change of viscosity with a change in temperature. A VI of 100 indicates a lower change in viscosity with a change in temperature. Amongst the mineral oils the highest natural viscosity index is obtained with paraffinic oils and the lowest with naphthenic oils. Oils with natural VI above 80 are called High Viscosity Index (HVI) oils, those below 30 are called Low Viscosity Index (LVI) oils and those of intermediate VI are Medium Viscosity Index (MVI) oils.

Oils of HVI are useful for machines operating over a wide range of temperatures and these are usually the better quality of manufactured oils. It is possible to increase the natural VI of an oil by dissolving a polymeric Viscosity Index Improver (VII) in it. These VI Improvers may be poly-isobutenes, polystyrenes or polyacrylics (eg. polymethyl-methacrylate, PMA) or various co-polymers. Most multi-grade oils such as 20W/50 are treated in this way and such oils may have VI values of much more than 100. When an oil contains a polymeric VI Improver, its apparent viscosity will depend on the rate at which it is being “sheared” or made to flow, as shown in Figure 8 below.

In the standard viscosity measurement techniques used for lubricating oils the shear rate is low, so that the quoted viscosities and derived SAE grades represent the behaviour of the oil at low shear rate. In a bearing, however, the shear rate may be very high, so the effective viscosity of a polymer containing oil will be much lower. One important consequence of this effect is that, on stopping an engine, the VI-improved oil drains away very slowly from the hot bearings, pistons, cylinder walls, etc., so that on restarting the engine a better lubricant film should be present, dependent upon the time interval.

**FIGURE 8.** EFFECT OF SHEAR RATE ON VISCOSITY. Source [13].



There is, however, a disadvantage. If the multi-grade oil is to have a viscosity at 0 °F equivalent to an SAE 20W oil, then the base oil must have a lower viscosity, as the viscosity will be increased by the polymer. When the oil is then sheared rapidly, it will behave as if its viscosity is the same as that of the base oil. In other words, in a high shear rate bearing at 210 °F the 20W/50 oil will be behaving, not as a SAE 50 oil, but as a SAE 10W or SAE 15W oil.

At low temperatures the viscosity of an oil may increase very rapidly, as the various liquid molecules approach their freezing points. With paraffinic mineral oils there is a tendency for waxy molecules to separate out and to thicken the oil into a grease or jelly. This tendency may be reduced by dewaxing the oil, or by adding a very small quantity of a polymeric "Pour Point Depressant" to it, see section 1.6.10.

### 1.6 Oil Additives and their uses.

Straight mineral oils produced by petroleum refining have properties which would usually satisfy the vast majority of industrial applications. It is possible to enhance certain (natural) properties of an oil by the incorporation of relatively small quantities of other materials, these being known as additives. Such substances must be soluble or dispersible in oil. Where the oil is likely to come into contact with water, as in steam engines or turbines, they must be insoluble in water otherwise they could be washed out of the oil.

The purpose of these additives is to improve the physical and chemical performance of the oil and to protect the engine from the harmful combustion products. The effect of an additive may be peculiar to the oil in which it is used, that is, an additive which is effective in one oil may not necessarily be as effective in another oil. Some additives assist each other, that is, they have a synergistic effect. Many additives perform more than one function, that is, they are multi-functional; for example, an anti-oxidant such as Zinc-Diethyl-Dithio-Phosphate (ZDDP) also acts as an anti-acid, extreme pressure and anti-wear additive. The effectiveness of an additive will vary according to the nature of the base stock. The ultimate criterion of a formulated oil, with regard to additive composition and concentration, is its suitability for its intended use and its performance in practice.

The increasing level of performance for contemporary internal combustion engines has required a progressive advance in the formulation technology of the available lubricating oils. As new engine designs demand higher specification oils so does the demand upon the role of chemical additives in the form of an additive package increases. Work on the development of oil additives during recent years has been

prolific, the resultant patent specifications have been numerous, and the chemistry of their manufacture often complex.

Most modern engine lubricating oils contain the following principal additive types:-

1. Anti-acids
2. Anti-oxidants
3. Anti-friction Compounds
4. Anti-wear Agents
5. Corrosion Inhibitors
6. Detergents
7. Dispersants
8. Viscosity Index Improvers
9. Extreme Pressure Additives
10. Pour Point Depressants
11. Anti-foaming Agents

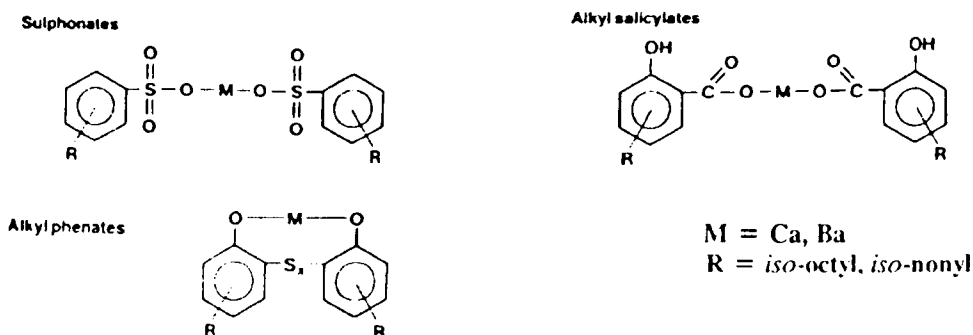
The classification of the additives in the list above categorises a particular additive property. In practice, some of the definitions are misleading and the boundaries between different classes often overlap. Each class of additive is discussed in greater detail below.

### 1.6.1 Anti-acids

A number of acidic compounds are formed during combustion, such as the sulphur and nitrogen oxides, hydrochloric and hydrobromic acids. The formation of sulphuric acid is prevalent in diesel engines using fuels containing sulphur in amounts ranging from 0.5 to 5%. These acids find their way into the crankcase via the “blow-by” from the combustion chambers. They can then cause serious degradation of the oil and engine components. Anti-acid additives are usually calcium, barium or magnesium carbonates, phenates, sulphonates and soaps, hence they are often classed as anti-oxidants and detergents as well. Detergents today usually contain a non-stoichiometric amount of metal compound in the ‘metallic soap’ (often 10 times the stoichiometric amount). For example, phenates and sulphonates can be ‘over-based’. This is achieved by the thermal reaction, in the presence of a catalyst, between an oil soluble sulphonate or phenate and a metallic base. The metal base forms a colloid (1nm - 1 $\mu$ m diameter), which can impart Base Numbers of around 300 to the additive.

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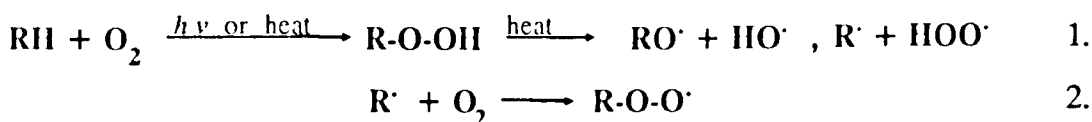
The Base Number of an oil is defined as the amount of acid required to neutralise the basic constituents in the oil. Blowby and acidic oil deterioration products, which would otherwise corrode bearings, can be effectively neutralised by these over-based detergents which form oil soluble or dispersible salts.



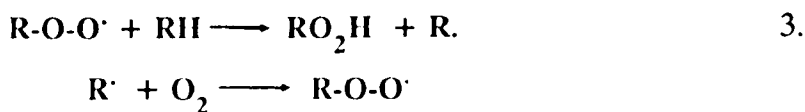
### 1.6.2 Anti-oxidants.

The main source of chemical breakdown is oxidation. Most of the chemicals present in lubricating oils react to a greater or lesser extent with atmospheric oxygen. Oxidation is accelerated by high temperatures (about 200 °C in the ring zone area) and the action of water and catalysts such as copper and ferrous metals. Hydroperoxides are produced when oxygen and hydrocarbons combine by a free radical mechanism:

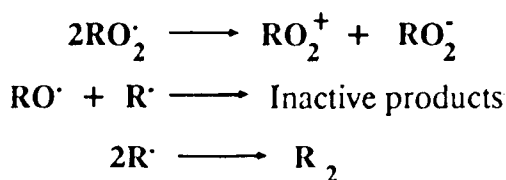
Initiation:



Propagation:

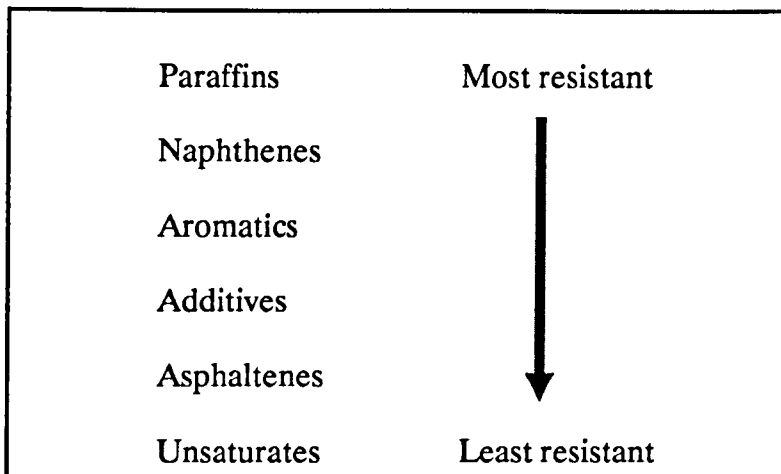


Termination:



The hydroperoxides decompose to form other materials that are more susceptible to oxidation. The rate of oxidation varies considerably between different compounds but, as a rule, the resistance to oxidation decreases as follows (Table 7):

**TABLE 7.** HYDROCARBON OXIDATION RESISTANCE. Source [13].



The effects of oxidation are a darkening of the oil, formation of lacquers, gums, varnishes, carbon particles and sludge deposits (which cause an increase in viscosity), and the formation of acids. Oxidation inhibitors are probably the most useful and widely used oil additives.

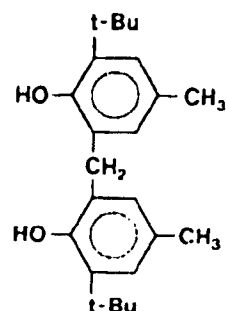
**TABLE 8.** COMMON ANTI-OXIDANTS. Source [13].

Type	Example
Metal organophosphates Amines	Zinc diethyl dithiophosphate Phenothiazine N-phenyl-naphthylamine Diphenylamine
Hindered phenols Organic phosphites Organometallics	2,6-di- <i>tert</i> -butyl-4-methylphenol Tri- <i>n</i> -butyl phosphite Zinc di- <i>n</i> -butyldithiocarbamate

The complete mechanism for oil oxidation is not fully understood. It appears to be a chain reaction. The first stage in the useful life of an oil is an induction period during which no apparent oxidation occurs. Organic peroxides are produced in the early stages of oxidation which then act as catalysts for further oxidation. Some oxidation inhibitors neutralise and prevent the formation of these peroxides; such anti-oxidants are called peroxide decomposers. Peroxide decomposers are compounds that can rapidly react with the hydroperoxide in such a way as to stop the free radical initiation process. Chain breaking anti-oxidants, such as phenols and aromatic amines, stop or

reduce the propagation steps (reactions 2 and 3 above). During later stages of oxidation fatty acids are formed indicating the depletion of anti-oxidants and the onset of rapid oxidation. Metal deactivators (anticatalysts) are required to render harmless soluble metal compounds (catalytic poisoning). These form protective coatings on exposed metal surfaces to further reduce oxidation of the oil. Some of the common anti-oxidants are listed in Table 8.

A typical 'hindered'  
*bis*- phenol



### 1.6.3 Anti-friction Compounds.

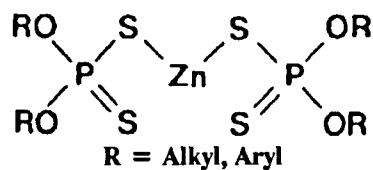
The basic purpose of the anti-friction compounds, known as friction modifiers, is to reduce the coefficient of friction between the surfaces of two rubbing solid bodies under boundary conditions. With about 1% mass of friction modifier in a formulated oil fuel economy benefits of 2-4% can be obtained. These additives have the property of lubricity or “oiliness”, as they have a high affinity for metal surfaces with which they form low friction films. These properties are readily associated with “fixed oils” such as castor, sperm and lard oils. Recently, jojoba oil has been introduced for this purpose.

Most compounds associated with “oiliness” have pronounced “wetting” characteristics and these are related to the phenomenon of “creep”. Creep is a function of surface tension at the fluid-metal interface. The “oiliness” factor is related to the size of the molecules which adhere to the metal surface as an ordered, absorbed, monolayer of polar chain molecules. The greater the ability of a substance to develop a monomolecular layer, the greater is its “oiliness” and its effectiveness as an anti-friction compound. The question of wear is not considered in relation to “oiliness” unless accompanied by another property associated with film strength under heavy or shock loads. Compounds used as “oiliness” additives include organic fatty acids and their esters, amines and other more or less acidic compounds containing oxygen, sulphur, halogens and phosphorus. Oleic acid reaches its maximum friction reducing effect when blended with mineral oil in quantities of about 3% by volume.



#### 1.6.4 Anti-wear Agents.

##### Zinc-Dithio-Dialkyl-Phosphate (ZDDP)



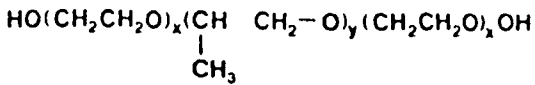
Friction is one of the causes of wear, and any reduction of friction, as discussed with “oiliness” additives above, results in a corresponding reduction in wear rate. This is true for certain conditions where there is accurate alignment, light loads, absence of shock, continuous running and near constant speed. However, “oiliness” additives lose their effectiveness at high temperatures, wear prevention agents act to reduce local temperatures. Anti-wear additives form anti-wear films as do extreme pressure additives with which they are often classed. Anti-wear additives have been found to produce a ‘chemical’ polishing at low temperatures such that the distribution of load is made somewhat uniform over a large surface area. Popular anti-wear additives are tri-cresyl phosphate and zinc dialkyl- dithiophosphate, the latter also being a good anti-oxidant. Generally the mechanism of the process is that a film is continuously formed by chemical action between the additive and the surface. This film is wiped away until well mated polished surfaces result. In this manner, the unit load is reduced to give better lubrication and thereby considerably retarding wear.

#### 1.6.5 Anti-corrosion Agents.

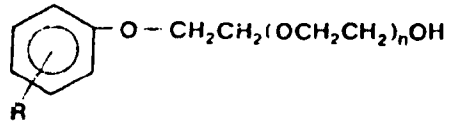
Corrosion is taken here to mean the etching of engine parts, particularly bearings, and it is chiefly caused by the acids formed during oil oxidation. The addition of anti-corrosion additives enhances corrosion inhibition by forming strongly adsorbed, protective film deposits on bearings and ferrous metal components. These films will be catalytically inactive, non-corrosive and have a strong affinity for the metal it is intended to protect. They will resist the washing effect of oil or other compounds. These additives break the chain reaction of oxidation and acid formation. Corrosion inhibitors may be sodium salts of sulphonic acids and esters of naphthenic acids. Zinc dithiophosphate and sulphurised compounds have also been successfully used. Overbased detergent additives usually provide adequate anti-corrosion protection but boosters of the type mentioned above give better protection.

The presence of water is responsible for the rusting of ferrous metals. When engines are run intermittently or are run cold, they are susceptible to condensation of water in the crankcase oils. Under these conditions the oil will become water-laden due to the condensed water not being evaporated. Rust preventative additives are compounds that will displace moisture already present and provide a film capable of

preventing any contact between the surfaces and surrounding moisture. This preferential wetting characteristic means that they are more surface active than water. Rust inhibitors which are extensively used are the polyglycol ethers. Metal sulphonates, amines, fatty acids, phosphates, metallic soaps, halogenated derivatives of fatty acids and oxidised waxes are also effective rust inhibitors. The use of these additives is restricted to protection of engines in storage. Petroleum oils themselves are good rust preventatives.



This is an EO/PO block copolymer in which  $x$  could be about 4 and  $y$  could be about 55.



This is an alkylphenol ethoxyethanol in which  $n = 4$  to 9 and  $R$  is often an iso-octyl or iso-nonyl group.

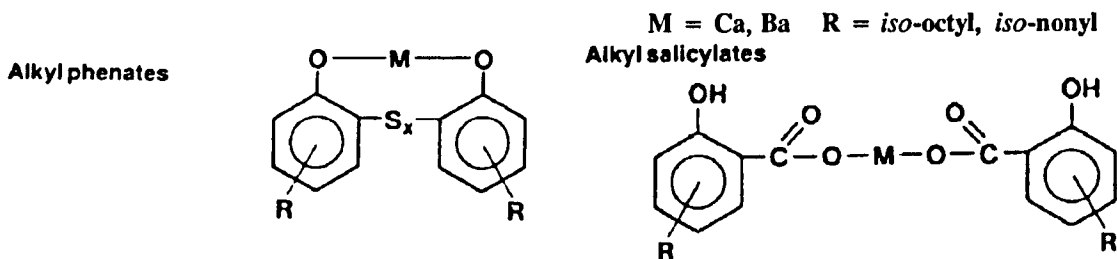
### 1.6.6 Detergents.

The name detergents can give rise to some misunderstanding; their function is not to act as an engine cleanser. These additives have nothing to do with lubrication; their function is to keep in suspension any dirt, carbon and wear debris that might otherwise collect on piston crowns, the piston ring area and in oil feed lines which would be detrimental to the function of the engine. In fact, an oil which had a purely detergent or cleansing action, if used in a dirty engine, could rapidly cause problems by removing deposits from some parts and depositing them in less desirable places such as oil-ways. It is for this reason that it is now common practice to refer to 'detergent-dispersant' additives.

Detergent oils are in demand for use in heavy-duty internal combustion engines, particularly high-speed diesel engines. Due to the higher compression ratios used, diesel engine piston/bore wall temperatures are generally much higher than those of similar sized petrol engines. Detergents are mainly intended to cope with the higher temperature oil deterioration and combustion products. They control the formation of deposits arising from high temperature oil oxidation, for example, they prevent the formation of varnishes and gummy products. Oxidation products originally appear as fine products that are insoluble to the parent oil, both as to solvency and washing effect. These particles ultimately agglomerate to form a tar-like sludge or like granular coffee grounds. Oxidation products deposited on the piston skirt develops into a hard, tenacious material resembling a lacquer or varnish as a result of baking at high temperature.

Metallic soaps such as calcium phenyl stearate were popular detergent additives at one time, but they were found to accelerate oxidation and cause bearing corrosion.

Metal salt detergents give ash deposits on decomposition, which is undesirable, and they do not perform well under comparatively low temperature 'stop-go' operation. The metals used also included barium, aluminium, magnesium, tin and zinc. The organic components include phosphates, sulphonates, carboxylates, phenolates and alcoholates. The use of purely organic detergents has resulted in lubricants of markedly superior performance. Metal-free polymers are used to decrease valve, ring zone and piston deposits, and eliminate oxidant-producing agents. These additives are ashless as they are non-metallic and leave no residue. Ashless detergents are polymerised olefins, or iso-olefins containing groups such as polyglycols, amides, pyrrolidones and carboxylic acids. Polymethylmethacrylate polymers function as detergents (and also as viscosity index improvers). The detergent activity has been found to increase with increasing molecular mass in the case of some groups of substances. A detergent additive may also have anti-oxidant and anti-corrosive properties. By combining detergents with oxyacids, the formation of lacquers can be reduced.



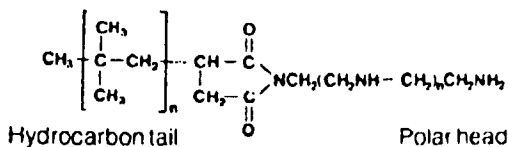
### 1.6.7 Dispersants.

Dispersants are additives that are used to keep wear debris, dust, oil decomposition products, soot, water and unburnt fuel in suspension in the oil as fine particles. Soot and lacquers tend to accumulate together to form large particles that may block oil-ways or filters. In general, however, dispersion of contaminants is less satisfactory than removing them. Dispersants function in the same way as detergents except that they are used for low temperature dispersion instead of high temperatures. Sludge and varnish deposits result largely from the products of incomplete combustion of the fuel which leak past the piston, are absorbed in the crankcase oil where they polymerise to give resins. The agglomeration of the resinous particles can be hindered by the use of compounds containing active groups of atoms such as carboxyl and hydroxyl groups, which are readily attracted to the surface of resins. The dispersed particles are small enough to preclude their separation from the parent oil although large agglomerates can be picked up by oil filters.

Organic polymers possessing polar groups such as in methacrylates, acrylates, alcoholates, carboxylates and polyalkenyl succinimides, are used as dispersants. The dispersant provides a characteristic film around the particle by polar forces, which repel other particles by an anionic electrical charge to prevent agglomeration.

### 1.6.8 Viscosity Index Improvers.

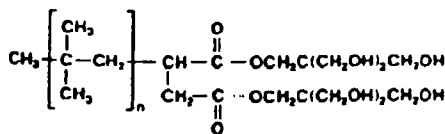
#### Mono-succinimides



These are usually prepared by reacting polyisobutenyl chloride with maleic anhydride and condensing the reaction product with a polyamine.

Viscosity index improvers are used for

#### Succinate esters



This PIB/MALA/PENTA type dispersant is an example of a succinate ester in which the polar head is obtained using pentaerythritol in place of the polyamine.

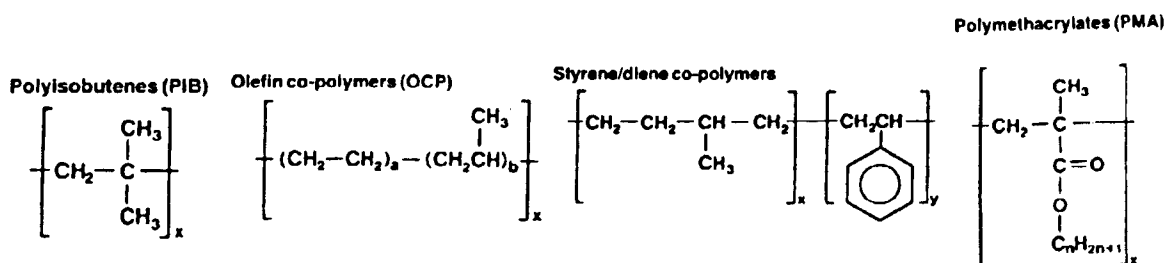
increasing the oils' viscosity at 98.9 °C (210 °F), leaving the viscosity at 37.9 °C (100 °F) relatively unaffected. The compounds in common use as viscosity index modifiers are poly-isobutene, polymethacrylate esters, and polyfumarate ester derivatives, between 1 and 5 per cent (by mass) being added to the oil. 'Paratone' is polyisobutene (C<sub>4</sub>H<sub>8</sub>)<sub>n</sub> where n varies from 180 to 270, the large size of the molecule being typical of viscosity index improvers. Such polymers have extremely high viscosities and the direct effects of their addition to the oil appear to be that they increase the viscosity of the oil at 98.9 °C to a proportionately greater extent than at 37.9 °C. This effect indicates that their solubility in oil increases with increasing temperature. The simple explanation is that at low temperatures the VII molecules are coiled and exist as a colloidal suspension in the oil. With an increase in temperature, the coils unwind, go into solution, and thus increase the viscosity of the oil. Another direct effect is that a given amount of VII gives a longer increase in viscosity in the case of oils of initially high viscosity than in oils of initially low viscosity.

The development of viscosity index improvers has led to the production of multi-grade motor oils. The 'Acryloid' or 'Plexol' range of additives consists of concentrates of methacrylate polymers in low viscosity, solvent refined, neutral oils. They are viscosity index improvers, pour point depressants, and also low temperature sludge dispersants. They are suitable for use in crankcase oils, automatic transmission fluids or hydraulic oils, the most suitable being selected according to the oil characteristic or combination of characteristics required to be improved. In the choice of any additive the points to be considered are:

1. The desired improvements in the characteristics of the oil required,

2. The solubility of the additive which may depend upon the type of base oil and its viscosity,
3. The concentration and type of additives already present in the oil,
4. The working temperature.

It should be noted that there is no advantage to be gained by using oils containing high molecular mass VII polymers in gear-boxes because the shearing action of the gears causes breakdown of the polymer chains. 'Pendant' groups (small branch groups) may be lost from the polymer chains. In fact, all polymer type additives will lose some of their effectiveness in service due to mechanical shearing of the polymer. This is known as 'shear-loss', and it depends upon the degree of shearing to which the oil is subjected, the molecular mass of the additive and its concentration in the oil. It can be reduced by decreasing the amount of additive used, or by using one of lower molecular mass.



### 1.6.9 Extreme Pressure Agents.

Extreme pressure (e.p.) additives are designed to react with exposed metal surfaces when boundary lubrication breaks down, usually under high pressure. They form compounds that will either sustain the load or shear easily and prevent welding and scuffing of the mating surfaces. Typical materials used as e.p. additives are organic sulphur, phosphorus and chlorine compounds that react with ferrous metals to form iron sulphides, phosphides and chlorides. The mechanism is thus a form of sacrificial corrosion designed to inhibit more severe damage. There are two types of e.p. additives:

- mild e.p. and,
- full e.p.

The latter react with bearing metals at normal ambient temperatures and thus should only be used in steel systems. Extreme pressure oils are principally intended for gear lubrication. Without them, hypoid gears, where tooth loading is heavy and the direction of sliding unfavourable to the formation of a fluid film, could not be used.

### 1.6.10 Pour Point Depressants.

Oils from paraffinic base crudes contain wax and hence have high pour points, but they generally have high viscosity indices. De-waxing is costly and may remove desirable constituents. When a paraffinic oil is cooled below its pour point, the wax separates out as needle-shaped crystals which join together to form a matrix. The oil is held in this matrix much as a sponge holds water, and thus ceases to behave as a fluid. This is undesirable if the engine is to start at low temperatures. Some pour point depressants function by surrounding the wax crystals with a protective coating such that further growth is inhibited. The crystals remain as small, individual crystals and the cold oil is then a pourable slurry. The growth of wax crystals is usually most rapid in one direction, and depressants can guide growth in different directions such that the harmful interlocking network is prevented from forming. Polymethacrylates are popular pour point depressants as well as viscosity index improvers. Other pour point depressants are alkylated waxes, polyalkylphenol esters, methacrylate and other high molecular mass polymers. The usual additive levels range from 0.01 to 0.3% by mass for a pour point reduction of about 20 °C.

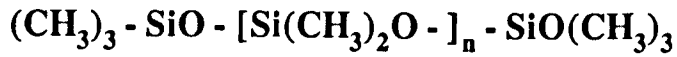
### 1.6.11 Anti-foaming Additives.

Any churning of the oil in the presence of air will encourage frothing or foaming. The greater the viscosity of the oil, the greater the tendency to foam. The presence of water encourages foaming, as do low temperature and high speed. Air enters the oil in several ways:

1. Through any pump intake not fully submerged in oil
2. By allowing oil to discharge into the reservoir or sump at a point above the oil surface
3. In a splash system, where oil is broken up into small droplets and then returned to the sump
4. Forceful ejection of oil from small orifices
5. Through turbulent stirring of the oil.

Foaming of a liquid is a surface tension effect and anti-foam agents function by reducing the surface tension of the oil, thus facilitating release of entrained air. Frothing can be overcome by the addition of minute quantities of a silicone, the most effective being the polymethyl-siloxanes used in concentrations of less than 0.001%. Adding larger amounts of anti-foam agents would be self-defeating because effective lubrication depends on the persistence of an oil film of high surface tension. Foam breakers are added to turbine oils, hydraulic oils, engine oils and other lubricant-

circulating systems. The most popular anti-foam agents are the polyorgano-silicones, such as polymethylsiloxane (shown below) .



Poly-methyl siloxane (n = 1 to 2000)

## 1.7 OIL ANALYSIS.

The specification for an important lubricant will often contain composition requirements, performance test requirements, and simple batch control tests. These specifications are often written to meet specific requirements and for particular applications. Specification limits as set out by purchasing contracts often become contractual obligations. No specification can be met without some type of approval testing. The sections that follow explain the various functional, performance and chemical testing that are most often encountered when testing engine lubricating oils.

### 1.7.1 Degradation and Testing of Oils.

Engine lubricants in general are required to operate under much more onerous and complex conditions than machine lubricants. Not only must they lubricate working parts satisfactorily, but they must do this under the relatively cool conditions prevailing in the crankcase and also in the high temperatures of the piston crowns and valve stems. In so doing, they are subject to considerable churning and oxidation. They also act as coolants in removing heat from under the piston. Oil finding its way into the combustion chamber may be thermally degraded or burned. Conditions may vary considerably from light automobile engines (which are themselves variable in speed and load) to aircraft engines. It is probable that no single laboratory test could assess the reaction of the oil to all such conditions. Reproducible and meaningful testing cannot be simulated except in real engines. Consequently, oil companies, government departments, research establishments and large users of vehicles have set up engine test laboratories. Engine testing of oils is confined to the requirements of petrol and diesel engines. Various engine tests have now been incorporated in oil specifications.

In attempting to differentiate between oils of different kinds, and specify the oils most suitable for definite applications, the usual approach has been to define the essential property or properties required of the oil for a given purpose and then find means of assessing that property or properties. Viscosity is the predominant factor in selecting the oil. Temperature effects, the results of oil deterioration, carbon deposit tendencies, etc., are subsidiary effects which become important in special cases.

Very few lubrication problems indeed are concerned with one variable only. Simple chemical and physical tests assess one property, often in arbitrary units. Where a number of such tests are involved, their interpretation and the relative stress to be placed on each can seriously complicate the selection of suitable oils. Therefore, while simple specification tests do provide some checks as to consistency of quality for batches of oils, in practice, they give little indication of the performance of a given oil.

Engine tests may be designed to assess or rate lubricating oil on the basis of one or more of the following as primary considerations, though other qualities may be reported upon:

Lacquer formation	Bearing corrosion
Sludge formation	Wear
Ring sticking	Engine cleanliness

Tests may be designed to test the quality of the base oil or to compare the qualities of formulated oils containing special additives. The general procedure is to select an oil which has given complete satisfaction in service to form a basis for comparison. Such an oil is referred to as a test reference oil. Test conditions will be such that as just to pass the reference oil and the criterion of the accuracy of the test must be the repeatability of the test on any test oil. Control of all temperatures, oil consumption and conditions is essential. Gruse and Livingstone [15] found that at low oil consumption paraffinic oils produced ring-sticking, while naphthenic oils left the rings free. At high oil consumption, naphthenic oils produced ring-sticking, while paraffinic oils left the rings free. A rise in oil consumption is probably indicative of the fact that ring-gumming has taken place.

It is essential that a proper running-in schedule should be followed before each test, the speed and engine duty (measured by brake mean effective pressure) being built up until test conditions are reached. The running-in should be done on the test oil and until the oil consumption remains reasonably constant, when running-in would be complete. After each test the engine has to be stripped down and the condition of each component reported upon. Test results are then compared with those obtained with the reference oil, the oils being graded as better, equal to, or worse than the reference oil. Some report methods include a point system whereby points are awarded for various bases of comparison, for example, the degree and colour of lacquer formation under the piston crown.



The engine should be reassembled after thoroughly cleaning it and new cylinder (or liner), pistons and piston rings fitted by selective assembly. New bearings should be fitted if bearing corrosion is being investigated. All clearances, ring gaps and ring wall pressures should be carefully checked and be within fine reproducible limits. It has been suggested that the continuous monitoring of the piston crown temperature is the best control temperature in oil rating tests. The temperature at the backs of the gas ring grooves is thought to be the best indicator for incipient ring-sticking.

### 1.7.2 A Review of Engine Testing of Lubricating Oils.

The world-wide engine testing scene of today is a vast subject and are of two main types, namely, in-house research procedures and the industry developed tests with written methods operated by a number of different laboratories. The in-house procedures vary from laboratory to laboratory, are restricted and confidential. The second category of industry wide engine tests, their historical development, primarily in the USA and Europe, is examined and linked to the current state of key tests. These are categorised into various types and consideration is given to the different levels of control and surveillance in the USA and Europe. Analysis of data published on the US sequence tests indicate where improvements have been made in precision and how some of these lessons may be applied to other procedures to provide improved testing in the future. Finally, a review of where engine testing may go in the next 5-10 years, is considered.

The first industry tests were developed in the USA, in the 1930's, in which the Caterpillar Tractor Company played a leading role in the development of lubricating oil engine tests. The main developments since then has been in the peripherals, that is, in controls, instrumentation and rating. On the instrumentation front the old type of instrumentation with large recorders and dial gauges have been replaced by the new type of digital displays based on printed circuit boards and integrated circuits yielding much more information. This technology when linked to modern control systems allows for better control and standardisation of test procedures.

Up to the 1930's, bench tests were considered adequate to determine the quality of lubricants but about that time considerable development work was carried out by Caterpillar and General Motors. The work done by Caterpillar is still largely recognised by the various procedures available today. The basic crankcase has not changed much since those days although changes have been made to other parts of the hardware and procedure to obtain more power and thus keep pace with the general increase in engine output. It was not until 1942 that the British Government recognised the need for engine testing in their specification DTD 472. However, by

that time the Americans were well on their way to developing specifications containing a number of engine tests.

The American Petroleum Institute and the Society of Automotive Engineers sponsored the Coordinating Research Council (C.R.C) to standardise the engine testing of lubricating oils. The C.R.C. issued five test procedures in 1943, using accumulated data and experience on standard engines. The C.R.C. test procedure designation L-1, L-2, and L-3 all used Caterpillar diesel engines to assess detergency, running-in characteristics and oxidation, and bearing corrosion tendencies, respectively. The L-4 test also assessed bearing corrosion tendencies but used a Chevrolet petrol engine, while test L-5 used a General Motors diesel engine to assess oxidation stability, bearing corrosion and detergency (500 hour test). Ultimately, only the L-1 and L-4 tests were found to be adequate and the other tests were omitted from specifications. In 1948, the introduction of a new level (Supplement 1) was made, which required the Caterpillar L-1 to be run on 1% sulphur fuel. In addition, at this time a significant increase in quality level was established called Series II which included for the first time a supercharged diesel requirement - the Caterpillar 1-D using a 1% sulphur fuel. In 1953, the numbering system was changed to the familiar MIL-L-2104 type designation. In 1958, the MIL-L-2104B specification was issued and it is at this stage that the present day multi-grade gasoline tests appear on the scene. At the same time the need for higher duty engine lubricants was accepted by the issuance of MIL-L-45199, requiring the Caterpillar 1-G and 1-D tests. This recognised the Series III level issued by Caterpillar in 1956. These specifications had quite a long life although there were changes in the tests and limits required which made it difficult to compare MIL-L-2104B lubricants qualified during the total life of the specification. The next major change took place in 1970 when the numbering system was revised to the present system. Thus, MIL-L-2104C and MIL-L-46152 were issued and have remained with until the present time, although, as with MIL-L-2104B, there have been modifications along the way to represent changes in the quality level required and to reflect the need to change specific engines as parts became unavailable. This again makes comparison difficult. A summary of the development of US Engine Test Specifications is given in Table 9.

As a result of the close co-operation of key US industry groups such as Caterpillar, Ford and GM together with the ASTM and CRC, the USA developed an effective range of specifications and test procedures to support them. In addition, the tests became relatively well controlled with reference fuels being required, a panel to review the test results and more recently the establishment of the Test Monitoring Centre (TMC) to organise reference testing and generally control the way laboratories run tests. No such parallel system developed in Europe, even allowing for the lag in

quality level and test development. The British Government's DEF specifications are well controlled and tighter than the American system, particularly in the area of the number of reruns allowed and the monitoring of the laboratories but it appears that the quality level now has little relevance for industry at large. Other European industry bodies such as IP, IFP, CEC and CCMC have all made significant contributions to the testing scene but overall agreement has not been reached on such things as tight control of fuel, laboratory installation and calibration, reference testing and review of results. This weakens the credibility of the various procedures and makes the comparison of results between laboratories less meaningful.

**TABLE 9:** SUMMARY OF DEVELOPMENT OF US ENGINE TEST SPECIFICATIONS. Source [16].

DATE	SPECIFICATION	TESTS
1943	US Army 2-104	L-1 (Caterpillar), L-4 (Chevrolet) L-2, L-3, L-5.
1944	US Army 2-104A	L-1, L-4
1949	US Army 2-104B Supplement 1	L-1 (1% S. Fuel), L-4
1950	US Army 2-104B Supplement 2	Caterpillar 1-D, L-4
1953	MIL-L-2104A with Supplements	
1958	MIL-L-2104	Caterpillar 1-H, L-38, LTDT Sequence I, II & IIID
1958	MIL-L-45199	Caterpillar 1-G, 1-D, L-38
1970	MIL-L-2104C	Caterpillar 1-G, 1-D, Sequence II, III, IV, L-31
1970	MIL-L-46152	Caterpillar 1-H, Sequence II, III, V, L-38

The other achievement in the USA is the willingness of the manufacturers to rely on each others tests which has avoided proliferation of procedures, although this situation may not hold for much longer in the heavy duty diesel area. Thus, although the US tests are relatively expensive to run in Europe, some UK laboratories do operate all the tests required by the MIL-L-46152 and 2104C specifications and fully participate in the industry groups in controlling and developing these tests.

The first British Standard Specification lubricating oil engine test was B.S. 1905 published in 1952. Two types of tests were specified; one for ring- sticking, piston lacquer deposit formation and piston and cylinder wear characteristics based on the C.R.C. L-1-545 specification in a 480 hour test. The second test was for oxidation and bearing corrosion characteristics based on C.R.C. test L-4-545 in a 36 hour test. The American procedures were followed very closely and all engine spare parts had to be imported. These tests were expensive and of long duration. The satisfactory completion of these tests was required for the approval of a lubricating oil under the United States Army Ordnance Specification MIL-0-2104, and the British Ministry of Defence Specification DEF 2101. In 1953, the Symposium of the Institute of Petroleum on the engine testing of lubricating oils, proposed a review on test engines available with the view to develop a British engine test.

As a result the Petter A.V.B. single cylinder four stroke diesel engine was put forward as a cheap small-scale test unit capable of giving preliminary screening tests of comparatively short duration of 120 hours. The Petter W.1. single cylinder four stroke spark ignition engine was adopted to replace the Chevrolet engine intended to assess the oxidation stability of oils and bearing corrosion. Extensive tests by the Institute of Petroleum had shown that the Petter W.1. and Chevrolet engines behaved in a similar way with regard to oil oxidation and bearing corrosion. Both the Ministry of Defence and the Institute of Petroleum thus accepted the Petter W.1. as a replacement for the Chevrolet engine. The Caterpillar engine test was retained for the assessment of ring-sticking, deposit formation and wear characteristics.

Other attempted test standardisation were undertaken, for example, with the Sunbury single cylinder gasoline engine, developed by BP under the auspices of the IP, together with the Shell/Ricardo diesel engine. These specific test engines were priced out of the market and the Petter engines took their place and have continued to the present day.

The Institute of Petroleum publication 'I.P. Standards for Petroleum and its products, Part III', is based on the work of the Engine Tests of Lubricants Panel and details four engine test methods together with the procedure for determining numerical ratings

of the engine components after the test.

Test I.P. 124/64 is basically equivalent to the C.R.C. L-1 test procedure and the Caterpillar A1 test, and is equivalent to the methods described in the DEF 2101-C and B.S. 1905:1965 specifications. It assesses the ability of an oil to prevent or reduce the formation of:

1. piston ring-groove deposits which may lead to ring-sticking,
2. cylinder deposits likely to lead to cutting of the top piston land,
3. excessive lacquer deposits on the piston,
4. piston ring and cylinder wear.

Test I.P. 173/60 is based on the Caterpillar D test and is intended to assess the same properties of the oil as I.P. 124, but with the engine running under super-charged conditions, and is claimed to evaluate oils for use in heavy duty internal combustion engines.

Test I.P. 175/64 is similar in purpose to method I.P. 124 and uses a modified Petter A.V.B. laboratory compression ignition engine in a 120 hour test with kerosene as coolant flowing in reverse to avoid excessive cylinder head temperature but giving raised piston temperature.

Test I.P. 176/64 uses a Petter W.1. spark ignition engine to assess oil oxidation, piston deposits and bearing corrosion of copper-lead bearing shells.

Until comparatively recently, there has not been strong co-ordination of engine test development in Europe and hence the procedures have not become so widely recognised and specified as those developed in the USA. The post war domination of the motor vehicle market by Ford and GM also contributed to the greater acceptance of the US test procedures.

At the present time, the USA situation appears to be relatively stable with the Sequence and Caterpillar tests dominating the world-wide quality scene. Very little proliferation of tests is likely in the gasoline area although new tests on smaller engines are being developed by GM to replace the IID and IIID, probably to run on lead free fuel. Similarly, a V-D replacement test is under development. Multicylinder diesel tests are being introduced with the Detroit Diesel 6V53T being required for the new MIL-L-2104D specification. Some proliferation of such tests appears likely with the Mack T-6, Caterpillar 3406 and Cummins NTC 400 already on the scene. A new Caterpillar procedure is being developed and likely to be in addition to the present

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tests.

In Europe, the reverse is true. Gasoline tests, in addition to the US sequence tests, are widely required by the different motor manufacturers and new ones such as the Daimler Benz M102E are being added. At present, the multicylinder diesel test picture is much more stable with the OM 616 and Tornado tests being the only well documented and having established procedures, although the OM352A is now being run by a number of laboratories. A summary of current industry engine tests is given in Table 10.

**TABLE 10.** CURRENT STATE OF INDUSTRY ENGINE TESTS. Source [16].

<b>TESTS WITH:</b>	Fully established method with surveillance group Laboratory calibration checks Regular reference tests Presented to review committees
CATERPILLAR 1-G	L-38
CATERPILLAR 1-H	PETTER W-1 *
SEQUENCE IID	PETTER AV-1 *
SEQUENCE IIID	PETTER AV-B 6
SEQUENCE VD	
*When run for DEF Specifications	
<b>TESTS WITH:</b>	Fully established method with surveillance group Reference fuel specification Reference oils available
TORNADO	PETTER W-1
OM 616	PETTER AV-1
FIAT 600D	PETTER AV-B
FIAT 124	MWM B
PEUGEOT 204	CORTINA/KENT
	VOLVO B-20

The wide variety of European gasoline tests will produce problems unless properly documented test procedures are established and/or reference fuels are brought under full control. The comparison of results from different laboratories will be unreliable and considerable expense with little end result is likely to be the overall outcome. Agreement on a small number of well controlled and monitored tests seems desirable but unlikely to be achieved in the short term. The CCMC have been working hard to achieve some measure of control, but individual manufacturers keep introducing new

tests and requiring lubricant manufacturers to run them if an oil is to be listed as a recommended lubricant.

The possibility of European and US requirements coming closer together is often discussed but appears very unlikely within the next 5-10 years for the reasons mentioned previously. If agreement cannot be established within Europe, it seems very unlikely that agreement will be achieved on a much wider issue involving even more loss of direct control.

As far as the tests themselves are concerned, improved instrumentation and control will be developed by individual laboratories within the framework of the present test procedures. These will be essential as researchers require more data from the very expensive tests and managers need to make decisions following a smaller number of tests. Again, however, close industry wide involvement will be essential to ensure that the tests run, still produce results in line with other laboratories unless the end product is for purely in-house research purposes. This problem is already causing concern in relation to the US sequence tests and at the recent ASTM meetings in Arizona, the ASTM Technical Guidance Committee charged the surveillance group chairman, together with the test sponsors, where appropriate, to have discussions with the TMC administrator and develop recommendations for data logging. In addition, a sub-group is to be set up to investigate different instrument practices and calibration procedures.

Thus, it is likely that new instrumentation and control developments will have to satisfy laid down standards and any laboratory deviating from these will be closely investigated before the modified test stands are qualified as referenced stands. Overall, engine tests have improved dramatically, particularly during the last six or seven years, but there is still a long way to go. With fuel and manpower costs increasing rapidly, engine testing will continue to be a very expensive, but very necessary part of lubricating oil and additive development. Apart from the large amount of money at risk from wasted tests, it must also be recognised that large commercial decisions, sometimes involving millions of pounds, may rest on results obtained from an engine test. It is, therefore, up to all those involved in the engine test business to produce tests which are meaningful, well controlled and which produce the maximum amount of useful data.

The precision of an engine test is affected by a number of different factors and can be quantified as follows:

$$\text{Variance (Rating) + Variance (Test operation) = Variance (Total)}$$

Test operation includes such things as fuel, build procedures and test operation, but it is difficult to obtain data to separate out these parameters. However, data are available on rating and total test precision from the various US tests to allow a reasonable estimate to be made of the actual part played by test operation and all that includes. Real improvements in rating precision have been made during the last ten years as a result of the activities of the various CRC rating workshops. These rating workshops are now an essential part of the system. In order to qualify as a rater for rating reference tests for submission to TMC, two out of three possible attendances per year at the appropriate symposia must be achieved.

In general, for parameters such as Caterpillar WTD, Rust, Sludge and IIID (% viscosity increase) engine tests, the standard deviation of results have been found to increase as the result worsens and this is true for both the overall result and rating.

The sequence IID test is a well controlled test with the overall variation in results being virtually explained by rating variance. This possibly surprising result may be due to the fact that if problems with this test occur with test operation, results vary widely from those expected and hence the test may have to be withdrawn or declared invalid due to operational reasons. This would mean the result would not be included in the statistics. Also, laboratories do take special care with reference tests and hence the result obtained may be more accurate than usual. Furthermore, more detailed analysis of results would indicate that not all of the variance of the individual rust ratings can be explained by rating variance alone.

In the case of the Caterpillars and the IIID very considerable variance may be attributed to test operations. This is best shown in the next table which summarises the standard deviation due to rating, test operation and total test, at key levels for the various tests. The precision of the viscosity measurements are so good that the standard deviation for this has been assumed as zero. Thus all the variance is in test operation. For example, at the 300 WTD level in the Caterpillar test, the standard deviation due to test operation is 115 and the viscosity increase standard deviation in the IIID at 350% is 94. Nevertheless, there is still room for considerable improvement if important decisions on the commercialisation of new additives are to be made in the shortest possible time and without many repeat tests. This whole question of test reproducibility is one of the reasons why full computer control on a range of key engine tests have increased in number, industry wide.



### 1.7.3 The Object of Lubricant Monitoring.

By taking a sample of oil from an engine (system) and examining it from time to time, a great deal can be learned about the condition of the oil and also of the engine (system). This information about the state and history of the oil can then be used as a basis for a number of decisions:

1. If the condition of the oil is very bad, this may indicate poor oil quality and may warrant immediate replacement.
2. If there are signs of oil breakdown, and the additives are becoming depleted, it may be possible to plan a convenient service for an oil change or system overhaul at some time in the near future.
3. If the oil and additives are not degraded, but there is either water present or solid or fuel contamination, it may be desirable to drain and “launder” the oil before returning it to the system.
4. If the oil is virtually as new, it may be possible to confidently delay the next service date.

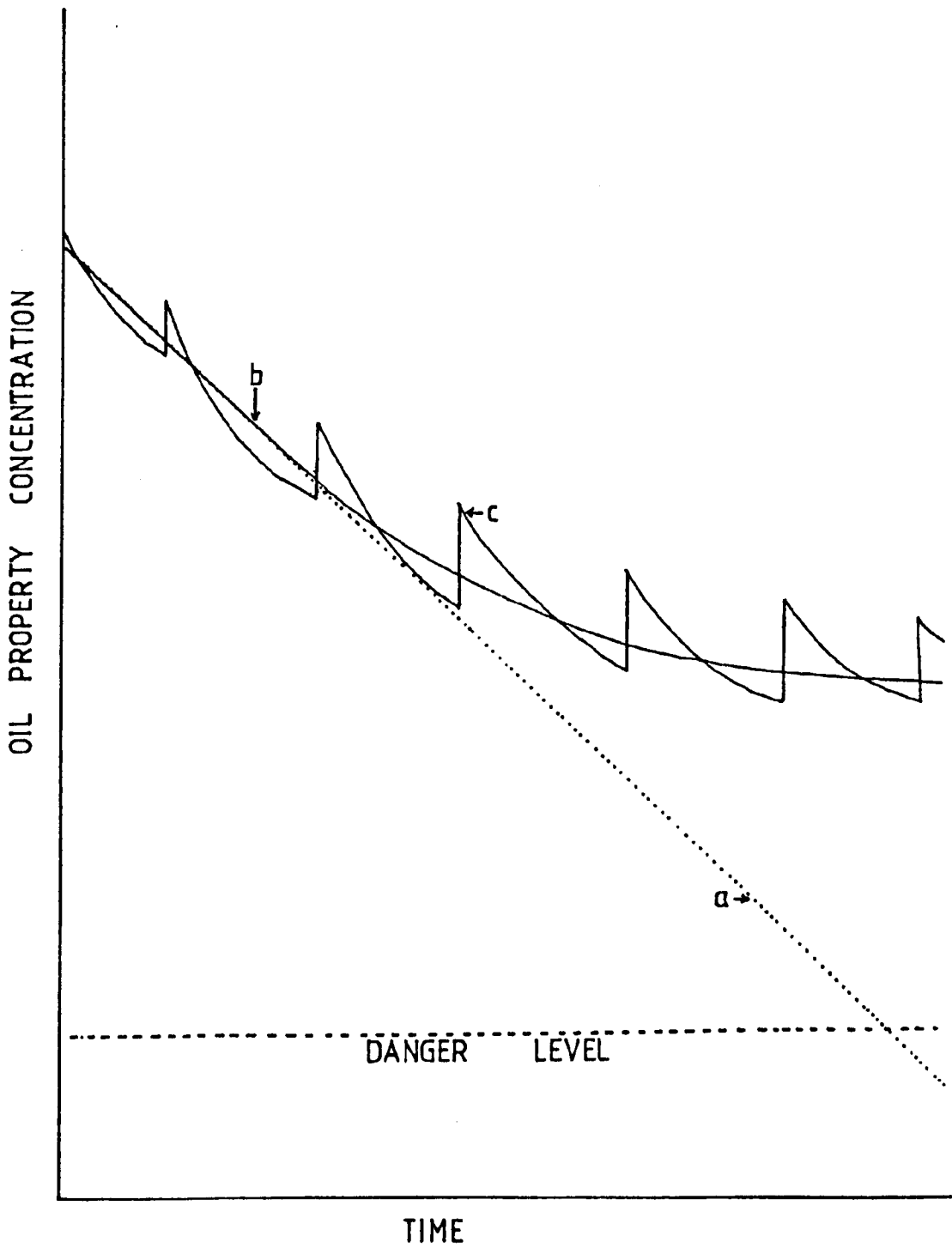
The testing of samples of engine oil makes it possible to use the oil:

1. More economically by draining it only when absolutely necessary and thus eliminates the need for fixed time or mileage service periods.
2. To assess the state of the engine and pinpoint component (impending) failures such that it may be possible to plan a system shut-down and overhaul at some convenient time in the near future. Thus system down-time and failure during operation can be reduced to a minimum.
3. To confidently produce a list of problem components and establish component and system life from past data.

Various models have been put forward for the consumption of lubricating oil in internal combustion engines, most recently the model of Yasutomi, Maeda and Maeda [17]. Their model is based on the two reactor model, one reactor is in the combustion zone of the engine which is a small but intensive reactor and the second being the relatively large sump reservoir which in reactor terms, is relatively benign. There must be some interaction between these two reactors as the oil is known to circulate to some extent between the sump and the top of the piston-ring pack. This kinetic treatment assumes a continuous decline in the lubricating oil components and properties, using the Marquardt equation [18], with service life of the oil and is based upon measurement of sump samples, Figure 9(a).

FIGURE 9. OIL ADDITIVE DEGRADATION BEHAVIOUR.

QUASI - CONTINUOUS STIRRED FLOW TANK REACTOR  
APPROACH TO ENGINE OIL DEGRADATION.



- a* = first order rate
- b* = theoretical continuous flow
- c* = regular batch/top-up

Marquadt Equation:  $X = X_0 - (X_\infty - X_0) \exp(-k_{1st} t)$

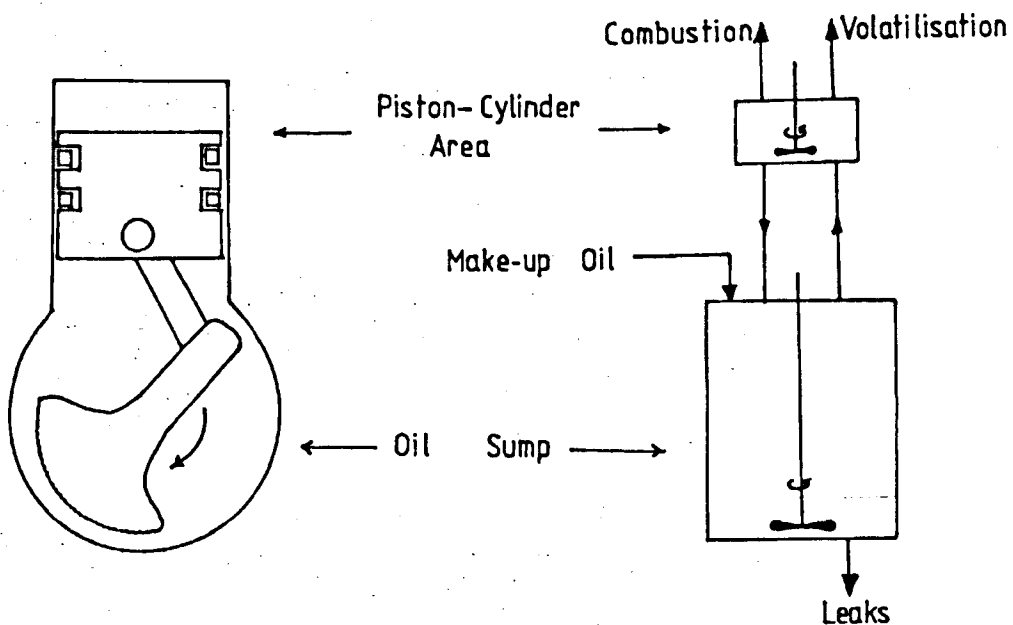
Eqn. 7

An alternative approach is based upon engine behaviour with 80% loading of designed performance under continuous operation where lubricating oil is lost by various mechanisms. These are, firstly, oil seepage from joints, seals, and shafts (total loss of both oil and additives), oil mist lost by breather recirculation (again, total oil loss), oil combustion (partial and selective oil loss) and oil volatilisation (selective loss of oil but not additive).

The overall rate of replenishment may be such that constant levels of oil properties result, in that the rate of degradation of the oil and additives is balanced by the rate of replenishment. The case is demonstrated by the plot of TBN against hours run, Figure 9(b). The increase in TBN towards longer hours run time results from the increased make-up with fresh oil due to the increased oil consumption experienced. This constant level of an oil parameter or component for intensive engine use is well established in other studies, for example, the Viscosity Index Improver concentrations in new and used oils. Where oil replenishment occurs discontinuously then the 'standing' oil property concentration will vary as a sawtooth pattern, Figure 9(c).

A better description of the system is that of a (quasi) Continuous Flow Stirred Tank Reactor (CFSTR) for the sump and an intensive, small reactor for the oil in the combustion zone (Figure 10) as set out below. This model is an extension of that from Yasutomi, Maeda and Maeda [17], allowing for the (quasi) continuous replenishment and constant oil/additive parameters. The prefix "quasi-" is used as the replenishment is not continuous as make-up occurs normally at 10 or 24 hour intervals. However, a continuous make-up constant head device with simultaneous oil consumption measurement has been developed.

**FIGURE 10.** CONTINUOUS FLOW STIRRED TANK REACTOR MODEL.



The current model is set out as a flow stirred tank reactor, (the sump) of volume,  $V$ , ( $\text{cm}^3$ ) with a replenishment flow of,  $U$ ,  $\text{cm}^3/\text{hr}$ . The kinetics of stirred tank reactors are well known from the original exposition by Denbigh [19] and the steady state concentration is given by the equation:

$$\text{rate} = \frac{d(C)}{dt} = (C_2 - C_1) \frac{U}{V}$$

Eqn. 8

The link to mechanical engineering is made by considering the lubricating oil distribution within the engine. One model is that of Dowson *et. al.* [20], which models oil transport up and down the bore through the oil scraper and compression piston-rings. The problem with this model is that it assumes that the oil to be of constant composition, which is not the case, as the results obtained by Bush [21] show, see Table 11, for oil samples obtained from the top-ring zone of a small air-cooled gas engine.

**TABLE 11.** DIFFERENCES BETWEEN NEW OIL, SUMP OIL AND TOP-RING OIL. Source: [21].

Oil Property	New oil	Sump oil	Top-ring zone oil
TBN (IP 177)	7.5	7.0	1.4
TAN (IP 177)	0	0	5.8
VII (by GPC)	100%	95%	50%
Distillation (GC)	100%	90%	27%
Oxidation Life/mins (by PDSC)	23	14	0
Oxidation (by IR)	0	0	0

What is not known are the rates of oil mass transfer between the two reactors; thus far only estimates have been reported. This transfer rate is to be determined in the near future. This model will then be developed further, after analysis of the oils obtained from the top-ring zone. The approach is an important conceptual framework to consider the oil component analysis which have been described above. The application is particularly relevant to the results obtained and reported, in that, firstly that the values for oil or additive will tend to a constant level and secondly, variation in levels will occur with the time of sampling relative to the time and amount of oil

that the values for oil or additive will tend to a constant level and secondly, variation in levels will occur with the time of sampling relative to the time and amount of oil make-up. This will be the case for an engine operating at high power levels with significant wear, giving a consequently high throughput of lubricating oil.

## 1.8 AIMS OF THE PROJECT.

An engine lubricant has become a critical component of modern, high performance engines and is often overlooked by engine manufacturers. The engine wear is closely linked to the lubricating oil quality during the service life of an engine.

The aim of this project were:

1. To examine the 'top end' mechanical wear in a single cylinder Petter AA1 diesel engine fuelled with a reference high sulphur diesel fuel.
2. To determine the degradation of a reference lubricating oil used in the diesel engine.
3. To develop new physical and chemical test techniques for new and used lubricating oils.

## CHAPTER 2.

### 2. OIL ANALYSIS.

#### 2.1 TOTAL BASE NUMBER (TBN).

The combustion of fuels produces acids. The combustion of sulphur-containing fuel produces sulphur oxides which, in the presence of water vapour, condense to form sulphur acids. Similarly, the use of lead scavengers in petrol, such as the chloro-bromo-alkenes, results in hydrochloric and hydrobromic acid formation. High temperatures and pressures during combustion in internal combustion engines result in significant production of nitrogen oxides which combine with water to give nitric/nitrous acids. These strong acids, if not neutralised, will diffuse into the lubricating oil of an engine and attack engine components, resulting in corrosive wear of bearings, cylinder liners and the valve train. Convenient ways of expressing the base or acid concentration in petroleum products are the Total Base Number (TBN) and Total Acid Number (TAN). A positive TBN value indicates the absence of strong acids. Engine lubricating oils are formulated with alkaline additives which will neutralise these acids. The majority of present day alkali additives are overbased (alkaline) metallic detergents. The Total Base Number (TBN) is a measure of the alkaline additive reserve present in the lubricating oil formulation. TBN is defined [22] in terms of the number of milligrams of potassium hydroxide which are chemically equivalent to the alkali that is present in 1 gramme of oil sample and is expressed as mg KOH/gm of oil.

Several methods for measuring TBN have been reported in the literature and the most widely used of these are summarised in Table 12.

Other methods of TBN determination have been proposed, such as that based on the use of concentrated sulphuric acid [23]. The TBN method using a propan-2-ol/toluene solvent mixture and hydrochloric acid as titrant was a proposed method in 1942 and served for a number of years. Through several revisions, it was published as an accepted IP method, designated IP 177/ASTM D-664, in 1964. However, serious discrepancies appeared when new additives were used. Many users modified the IP 177 version by using a back titration or a variation using acetic acid/chlorobenzene as a solvent medium and perchloric acid as titrant. The full text of the latter method was proposed in IP standards in 1969 and as a Tentative Standard Method IP276/ASTM D2896, in 1971, and subsequently accepted as a full standard.

**TABLE 12.** TBN DETERMINATION TECHNIQUES AND METHODS. Source [27].

Technique	Method, Medium, Titrant	Comments.
e.m.f.[22]	IP 177/ASTM D664. Solvent mixture of toluene/water/propan-2-ol  Titrant: KOH in propan-2-ol	No inflection point for used oils. Lengthy titration time. Incomplete neutralisation Affected by water content.
e.m.f [22]	IP 276. Solvent mixture of chlorobenzene/glacial acetic acid. Titrant: HClO <sub>4</sub> in glacial acetic acid	Rapid equilibrium. Sharp break at the end point. Clear inflection obtained.
High-frequency [24]	IP 177 solvent HCl in propan-2-ol	Reduced analysis time. Sharp break at end point. Eliminates electrode contamination
Conductivity [25]	IP 177 solvent	Sharp break at end point Eliminates electrode contamination. Less time consuming. Buffer solution eliminated.
Calorimetry [26]	IP 177 solvent and titrant	Eliminates contamination of electrode. Less time consuming. Is simpler.

The essential differences between the ASTM D664/IP 177 and ASTM D2896/IP276 test methods is shown in Table 13. The main point to note is that the acid used in IP 177 is hydrochloric acid, whereas, in IP 276 perchloric acid is used. These acids are 'strong' acids of comparable strength in water, but in non-aqueous solution, as used for the TBN determinations, perchloric acid is much the stronger acid. The IP 177 method has been found to give low results, with poor repeatability, for many additives, particular for used oils. Low results have been obtained for highly over-based products and those containing nitrogenous polymeric dispersants. For chlorobenzene-acetic acid solvent media, all bases weaker than the acetate ion can have no inflection in the titration curves. Perchloric acid is, therefore, capable of rapid and complete neutralisation of weak bases (for example, succinimide dispersants) which the hydrochloric acid may otherwise fail to neutralise or interacts only very slowly with them resulting in poorly defined inflections. The TBN values obtained by

the IP 276 method are often higher than those obtained by IP 177. Differentiation between TBN values is observed when samples contain additives with different basicity, for example calcium sulphonate, carbonate and hydroxide [23]. Hooks' [28] results for TBN determinations of diesel engine oil using three different acids, perchloric, sulphuric and hydrochloric acids in chlorobenzene/acetic acid and toluene/propan-2-ol/water media respectively, shows three curves with decreasing TBN values from perchloric, sulphuric to hydrochloric acid, respectively.

High frequency oscillator procedures have been used to determine TBN and TAN, giving sharp breaks at the end point, indicating values comparable with those obtained potentiometrically [25 and 29]. The method of conductimetric analysis in propanol/toluene/water in titrating new and used samples of oil [30] and in a benzene/alcohol solvent medium in titrating phenolates and sulphonates has been found satisfactory. However, as benzene is a Class A carcinogen, it is no longer used in open laboratories. Conventional thermometric titrimetry was used to determine acids and bases in light and heavy petroleum derivatives, including lubricating oil [31], crude oils [24] and petroleum distillates [32, 33]. Studies [34] show that the acids in the oils not determined by the thermometric method are weaker than  $pK_a(H_2O) = 10$ . Thermometric titration values are comparable with the standard methods of determination of TBN and TAN.

More recently [34], attention has been given to the application of a tri-solvent system containing chloroform for TBN determination. Chloroform, as a carcinogen, will be replaced by a more acceptable chlorinated solvent such as trichloroethene ("trike"). Replacement of chloroform by trichloroethene requires re-validation of the trichloroethene system. Values obtained for the TBN of an oil sample are generally higher than those obtained using IP standard potentiometric methods.

Acid or base character is not an absolute property of the solute but can only be specified in relation to the solvent used. The ability of a liquid to dissolve ionic compounds depends strongly, although not exclusively, on its dielectric constant (permittivity). The acidity of any aqueous system is limited by the fact that the strongest acid that can exist in the presence of water is  $H_3O^+$ . Any stronger acid simply transfers its protons to  $H_2O$  to form  $H_3O^+$ . A base in an 'acidic' medium will be more reactive than that in water as water has a great 'levelling-up effect' on acid and base strengths due to the large solvation effects of water resulting from its high permittivity. The range of acid and base strengths in water are, therefore, restricted; this restriction will be removed in solvents of much lower permittivity, giving much wider ranges of acid and base strength. A base in an 'acidic' solvent will be more reactive than when it reacts in aqueous solution. Thus, an acid which is stronger in



low permittivity, non-aqueous solvents will titrate weaker bases and thus give a different TBN value to that obtained by using another, weaker acid. There are a number of liquids that are considerably more acidic than concentrated solutions of nitric and sulphuric acids, by as much as  $10^{+6}$  to  $10^{+10}$  times in the case of super acids, e.g. fluorosulphonic acid. Acid-base interaction in non-aqueous solvents are best understood by defining an acid as an electron pair acceptor and a base as an electron pair donor - the Lewis acid base definition. Protic solvents, e.g.  $H_2O$ ,  $NH_3$ ,  $HF$ ,  $HCN$ ,  $H_2SO_4$  undergo autodissociation and supply  $H^+$  to stronger bases than their corresponding deprotonated species. Perchloric acid has only a single proton and four oxygen atoms around the central chlorine atom which, on auto-dissociation, forms a very stable anion due to the very effective delocalisation of the negative charge on the perchlorate anion. In the IP 276 titration solvent of glacial acetic acid and chlorobenzene, the strongest acid that can exist would be  $H_3C^+CO_2H$ . In the IP 177 titration solvent of isopropanol, water and toluene, the strongest acid is  $H_3O^+$ . The  $H_3C^+CO_2H$  is the "stronger" Lewis acid than  $H_3O^+$  and would, therefore, be capable of neutralising those weak bases which are not neutralised by  $H_3O^+$ . Therefore, the acid strength range of the IP 276 solvent would be larger than that of the IP 177 solvent. The TBN values obtained by IP 276 are, therefore, usually higher than that obtained by IP177, even for new oils.

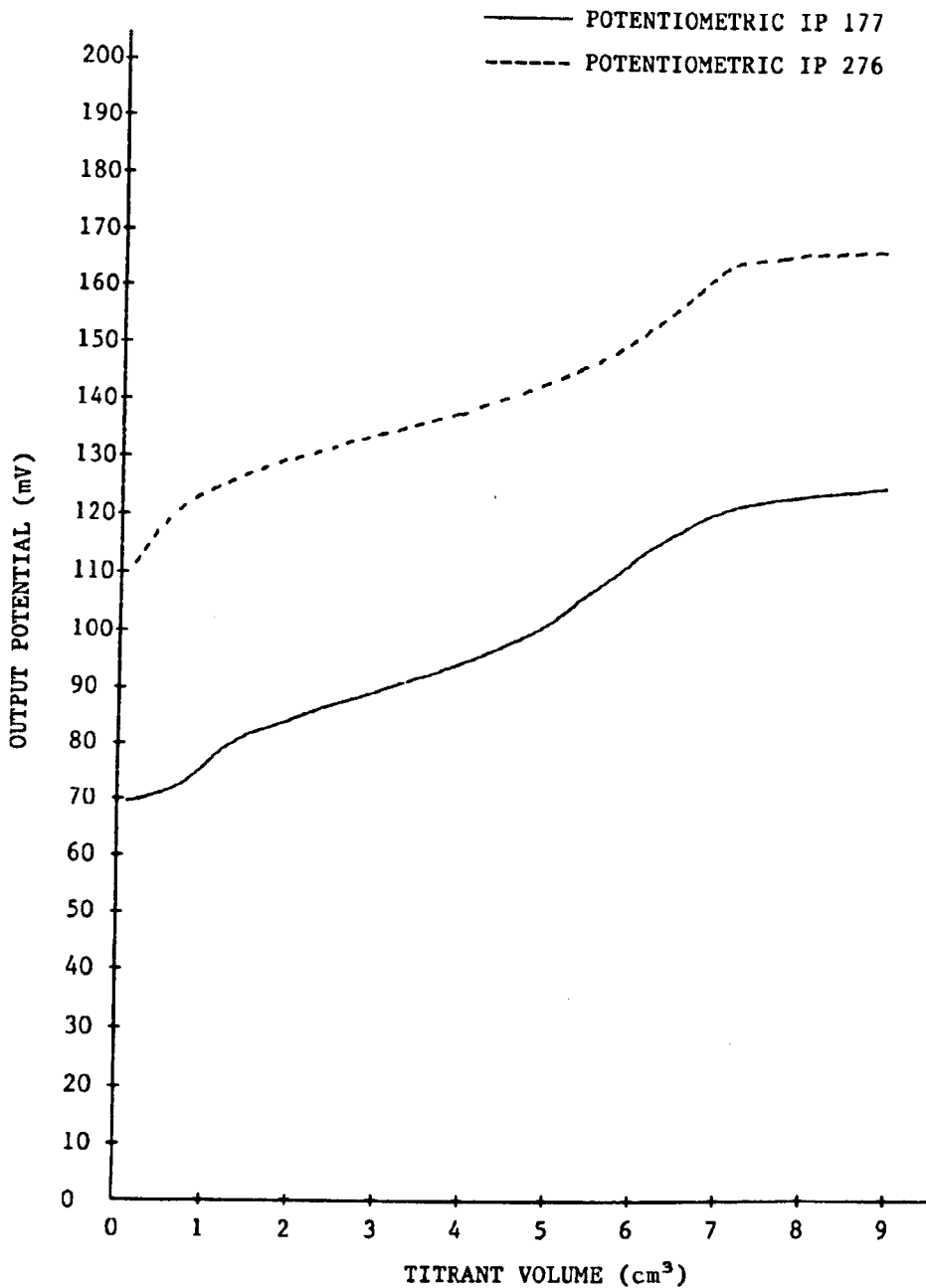
The progress of the titrations of the IP 177 and IP 276 TBN determinations is followed potentiometrically using glass and calomel electrodes. These electrodes are prone to contamination and need frequent replacement. In addition, these electrodes need frequent conditioning and require considerable time to equilibrate. The quality of results obtained from these determinations is often poor, as the sigmoidal titration curve becomes flat and indistinct, particularly for used oils, Figure 11. The problem lies in the interpretation of the mid-point of the sigmoidal plot of electrochemical potential against titrant volume. For most new oils a smooth curve is obtained which has a readily defined end-point at the mid-point of a sigmoidal curve (Figure 11). For used oils, the definition of the titration curve gradually degrades, becoming more and more diffuse with increase in the service life of the oil, making the end-point definition more difficult. Eventually, an inflection point cannot be observed and a back titration or buffer end-point method must then be used, as defined by the Institute of Petroleum, giving wide error bands that are acceptable for reproducibility (see Table 14). It is probable that the chemical species being titrated in used oils have a spread of alkalinity values, in contrast to the much more homogeneous species (pure additives) in new oils. Used oils, therefore, must consist of a large number of different basic constituents, ranging from the strong metallic bases (hydroxides, carbonates, and soaps), through to ashless detergents and numerous weak bases and salts arising from the degradation of the two former additive types.

**TABLE 13. DIFFERENCES BETWEEN IP 177 AND IP 276 TESTS.**

	IP 177 (ASTM D664)	IP 276 (ASTM D2896)
Titration Acid	Hydrochloric	Perchloric
Solvent	Toluene Propan-2-ol, Water	Acetic Acid Chlorobenzene Acetic Anhydride
Titrant	0.1N HCl in Propan-2-ol	0.1N HClO <sub>4</sub> , in Anh.Acetic Acid.
Repeatability	Poor	Good
Blank Titration	Required	Required
End point Determination	Buffer end point	Back Titration for used oils
Applicability	New Oils only Does not work for used oils	New Oils only Does not work well for used oils
Toxicity	Not a problem	Precaution needed

The following general guidelines have been proposed by the IP for quantifying the potentiometric end-point. The inflection point marks the titration end-point and is generally recognised by inspection of the potential versus volume titrant added curve. This is evaluated as whenever at least five successive cell potential changes, caused by the addition of five 0.05 ml increments of titrant, produce a cell potential change greater than 0.015 V and is at least 30% greater than that produced by previous or subsequent additions. The inflection point is normally placed between the cell voltages representing the non-aqueous acidic and basic buffers. If an inflection appears in the potential region between the acidic buffer potential and a point 100 mV past that potential, then this point is taken as the end point. If no inflection can be found then the end point is taken as the point on the curve that corresponds to the acidic buffer potential. See Figure 12 for examples of end-point determinations.

**FIGURE 11.** TYPICAL POTENTIOMETRIC TITRATION CURVES.



A further problem of end-point determination, of the two IP/ASTM TBN test methods, is the reproducibility of the results. Reproducibility is defined as the same result for a given oil sample by different people using the same type of apparatus. Similarly, the repeatability of obtaining the same result, that is, the results obtained by one person using the same apparatus, is often difficult. This is particularly the case for used oils. The IP/ASTM [22] guidelines for precision of results obtained in titration curves with good inflection points is shown in Table 14, below.

Pawlak, Fox *et.al.* [21] have shown that acid-base “neutralisation” in non- aqueous solution can be spread over a large range of  $pK_a$  dependent upon the nature of both the acid and of the base, the solvent, and the nature of the proton transfer, i.e., complete transfer from  $AH^+$  to B, or a bridged structure,  $A^-H^+B$ . These effects contribute to the differences obtained for TBN values from IP 177 and IP 276, where acids of different strengths are used which react with different ranges of basicity.

**TABLE 14.** IP TBN ACCEPTABILITY LIMITS (All values are in mg/g oil). Source [22].

Acid or Base Number	Repeatability	Reproducibility
0.05 to 1.00	0.02	0.04
1.0 to 5.0	0.1	0.2
5.0 to 20.0	0.5	1.0
20.0 to 100	2.0	4.0
100.0 to 250	5.0	10.0

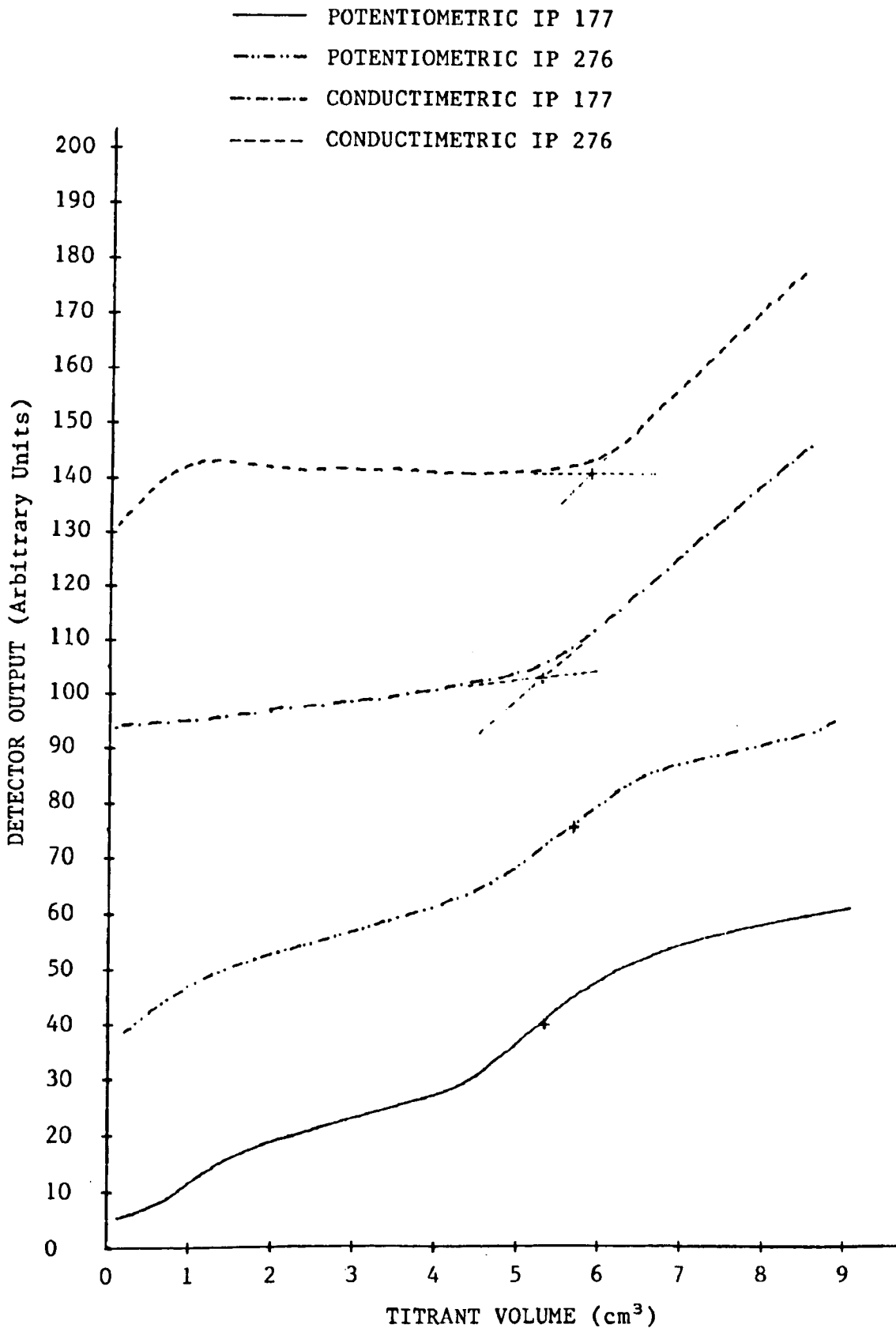
When poor or undefined inflections are obtained in the titration curves, the values for repeatability and reproducibility will be larger than those indicated in the Table 14, above. In practice, for used oils of varying degrees of degradation, it is usually necessary to carry out back-titration, in order that a satisfactory end-point is obtained. The application of two alternative techniques to determine the TBN for either of the two IP/ASTM standards causes confusion and concern. Some knowledge of the history or origin of the samples is, therefore, required to minimise wastage of time and resources. The IP/ASTM guidelines for the reproducibility of used oils allows for the variation in TBN values in the range 10% to 80%. These factors do not allow for an automated process, except if all the used oils are to be back-titrated for TBN determinations.

The equilibration times between additions of titrant have an effect on the TBN result obtained. An equilibration period of 90 seconds between titrant additions of 0.1 ml can lead to titrations of one per hour based on a maximum titrant volume of 4 mls. Such slow titrations are, therefore, tedious and inefficient with respect to time, equipment and resources. Time savings can be achieved by rapid titrant addition until a given potential is reached or by reducing the sample mass, with some loss in precision.

This multitude of different applicable test methods and the difficulty of obtaining reasonable end-points, does not make the automation of Total Base Number determination easy. It was, therefore, necessary to find a better method of

determining the Total Base Number of lubricating oils.

FIGURE 12. EXAMPLES OF END-POINT DETERMINATION.



## 2.2 TOTAL ACID NUMBER (TAN).

The Total Acid Number is defined [20] as the quantity of base, expressed in milligrams of potassium hydroxide, that is required to neutralise all acidic constituents present in 1.00 gramme of oil. Alternatively, the TAN is equivalent to a quantitative titration required to raise the “pH” of the sample to 11. The “Strong Acid Number” (SAN), refers to the quantitative titration with KOH required to bring the sample “pH” to 4. The weak acids and the effect of some additives are indicated by the difference between TAN and SAN. The determination of the Total Acid Number (TAN) has been a standard test specification for unused straight (i.e. without additives) mineral oils. The object is to check that:

1. Naturally occurring acids have been removed during refining, and
2. Acids used in the course of refining are not present in the finished oil.

New, highly refined straight mineral oils have a TAN (neutralisation) number of 0.10 mg KOH/g, or less. Formulated lubricating oils containing fatty acids, metallic detergents and acidic organic compounds may possess significant Total Acid Numbers, typically 0.3 mg KOH/g, even though no free acid is actually present. Used lubricating oils may show lower TAN values compared to that originally present. Used oils with higher TAN values indicate that the oil has depleted its TBN reserve and accelerated wear rates, due to corrosion, are imminent.

High TAN values would arise due to oil oxidative, organic, degradation products, depletion of TBN reserves by acidic, inorganic, combustion products and the eventual predominant acid levels from the combination of these acids. In diesel engines, a Total Acid Number of up to 4 mg KOH/g can be tolerated, above which oil oxidation may proceed more rapidly [32]. Regular determination of the oil's Total Acid Number therefore provides a useful indication of the quality of the oil in order to extend its life in the engine.

Direct titration of an oil by an aqueous solution is difficult due to the immiscibility of oil in water. Emulsions may be formed and colour indicators cannot be noticed in dark coloured mixtures. These difficulties are overcome by dissolving the oil in a solvent consisting of toluene (50% v/v), anhydrous propan-2-ol (49.5%) and water (0.5%). This solution is titrated against a standard 0.1N alcoholic potassium hydroxide solution using a potentiometric titration. The end-point is the point of inflection in the sigmoidal curve in the plot of electrode potential against volume titrant added.

There are a number of variations of the above method for Total Acid Number determination which forms the basis of the ASTM D664-58 and IP 177 tests. These

potentiometric titrations in non-aqueous media suffer from similar difficulties in obtaining clear end-points along with the problems of electrode contamination, conditioning and short life as experienced by that in Total Base Number determination. A better end-point indicator system was, therefore, sought.

### 2.3 OIL VISCOSITY.

The most important physical property of a fluid lubricant is its viscosity. The viscosity of a liquid can be most simply defined as its resistance to flow, and is a measure of the friction of the fluid molecules when moving past each other. A freely flowing liquid such as water has a low viscosity whereas a thick syrup has a high viscosity.

Viscosity is measured in several units, and the relationship between the common units has been given in Table 5, see Chapter 1. The regular determination of an oil's viscosity and its variation against operating engine hours can be used as an indicator of the oils quality for its continued use and can indicate severe cases of oxidation, sludge formation or fuel dilution.

Kinematic Viscosity,  $\nu$ , is a measure of the resistance to gravity flow of a fluid, the pressure head being proportional to its density,  $\rho$ . For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity  $\nu = \eta/\rho$ , where  $\eta$  is the dynamic viscosity coefficient. The cgs unit of kinematic viscosity is one centimetre (squared) per second and is called one Stokes (St). The IP standard for viscosity measurement (IP 71) employs a capillary viscometer and requires accurate temperature control. This type of viscosity measurement is slow and the cleaning of the viscometers can be difficult, especially when large numbers of used oil samples are to be tested.

Dynamic Viscosity,  $\eta$ , is the ratio between the applied shear stress and rate of shear. The cgs unit of dynamic viscosity is one gram per centimetre per second and is called one poise (P). The IP standard dynamic viscosity is calculated from the kinematic viscosity and the density of the sample and, therefore, has the added complication of determining the latter parameter.

The dynamic viscosity of an oil can be easily and accurately measured by the rotating disc apparatus. A rotating disc and cone viscometer, that requires small quantities of oil sample, is used to determine the viscosity of the lubricating oil. The viscosity is determined over a wide range of speeds at the three standard temperatures (namely 0, 100 and 210 °F) in order to calculate any change in Viscosity Index (VII). This method of viscosity measurement allows the viscosity change at high shear rates to be

ascertained and is indicative of the conditions experienced in the engine.

## 2.4 ADDITIVE AND WEAR METALS.

The metallic content of an oil can be obtained by ashing, ferrographic analysis and spectrographic analysis. The quickest and most accurate method is the spectrographic analysis which was first investigated by American Railways in 1954. It was found to give a very useful early indication of failures of railway diesel engines which could be withdrawn from service for overhaul in time to avoid any catastrophes or disruption during operation. The technique was extended to the USAF in 1955 and by 1968 the USAF replaced scheduled jet aircraft engine overhaul with "On-condition Overhaul" based on regular Spectrometric Oil Analysis. By 1970 Spectrometric Oil Analysis was being used regularly by most air forces and by 1980, most airlines had followed suit. The technique has found application in naval vessels as well as ships.

The two main instruments used in spectrographic oil analysis are the Emission and Atomic Absorption Spectrometers. Both depend on the fact that when metal atoms are excited, such as by heating, their different energy states are separated by steps (quanta) of particular frequency or wavelength which are characteristic of the different metals. In the emission spectrograph a sample is ignited by an electric arc from a carbon electrode. The light intensity at the characteristic frequencies is proportional to the concentration of each element. In the latest technology, plasma sources are used to excite the atoms. In Atomic Absorption a sample is burnt in an acetylene or nitrous oxide flame. A concentrated beam of light is passed through the flame, and some of the light is absorbed at frequencies characteristic of the metal elements present. The amount of absorption at the characteristic frequency depends on the concentration of the element present in the oil sample. The metal elements that are of interest to the engineer include calcium, zinc, iron, magnesium, aluminium, chromium, copper, lead, and sodium. Non-metals such as sulphur, silicon and phosphorus are also of interest to the engineer.

The metal content of the oil can be as large as several percent for additive metals or as small as a few parts per million for wear metals. To avoid erroneous readings due to the presence of large particles of wear debris, the oil sample must be filtered such that only finely divided metals, metal oxides and organo-metallics are analysed. An individual spectrographic metal analysis is of little value. The value of spectrographic analysis lies in the continuous monitoring and trend analysis of the data, comparing the new data with that of the new oil and that of the previous tests, in order to note deviations that are indicative of potential, imminent failures. The technique of spectrographic oil analysis requires minute amounts of sample and is fairly cheap. The



main drawback of spectrographic analysis is that the exact source of metals and certain types mechanical damage cannot be distinguished. The results obtained by spectrographic analysis has been assessed as being reliable between 90% and 98%, by various users [13].

A number of IP methods exist for the determination of additive and wear elements, most of which require wet-chemical analysis. The spectrographic technique can elucidate, simultaneously, several elements from the same oil sample.

## 2.5 OIL OXIDATION.

The most important type of chemical reaction affecting oils in service is oxidation, which very often determines its service life. The effect of oxidation is to introduce oxygen atoms into the hydrocarbon molecules of the oil, to produce aldehydes, acids and highly oxidised gums, lacquers and solids residues. Oxidation rates can be accelerated in the absence of anti-oxidants, at high temperature, acids and those metals that have a catalytic effect on oxidation. Oxidation products cause corrosion of bearings and other surfaces and may result in increasing viscosity, sludges and coatings on various surfaces.

The IP 48 test method for the oxidation of lubricating oil involves heating the oil at 200 °C in an air stream, for two 6 hour periods followed by a kinematic viscosity (at 40 °C) and Ramsbottom carbon residue test ([22], IP 14) on the oxidised sample. These results are compared with that of the new oils. The ratio between the oxidised over the new oil parameters is used to assess the oxidation resistance quality of the oil. This type of testing is very time-consuming and cannot be used to test a large number of samples without a large amount of resources and equipment.

A rapid, alternative test method based on Pressure Differential Scanning Calorimetry has been evaluated to determine the oxidation resistance of lubricating oils. Many oxidation products contain a carbonyl group,  $>C=O$ , in which a carbon atom is linked to an oxygen atom by a double bond. The carbonyl group produces a characteristic absorption band (at about  $1700\text{ cm}^{-1}$ ) in the infrared spectrum and can serve as a quick check for oxidation.

## 2.6 VISCOSITY INDEX IMPROVERS.

The IP 226 standard test method is based on the kinematic viscosity of the oil at 40 °C and 100 °C (IP 71) as described in section 2.3 above. The calculation and Tables are provided in the IP test procedure [22] in order to determine the Viscosity Index of an

oil.

The Viscosity Index Improver (VII) in certain lubricating oil is polymethylmethacrylate (PMA) with an average molecular mass of 270,000 g/mol. In service use, the VII will be degraded with a resulting decrease in molecular mass. Two properties are important, namely, the change in the concentration of VII in the oil with service life and the VII molecular mass distribution. The VII can be separated from the oil and measured by gel permeation chromatography (GPC).

## 2.7 OIL VOLATILITY.

Lubricating oils are not generally volatile, and it is only with low viscosity oils at high temperatures or in vacuum applications that evaporation is likely to be significant. Its effect is to increase the viscosity of the oil. The IP 45 test method for flux oil loss requires the oil to be heated at 162 to 164 °C for 5 hours. Such a thermo-gravimetric test is slow and is better suited for the determination of fuel and water present in oils. This method was investigated for determining fuel dilution of the oil.

## 2.8 DETERGENCY AND DISPERSANCY OF OILS.

There is no IP test method for the determination of detergents or dispersants. There is a blotting paper test which is used in assessing dirt levels in used oils. The policy that it is better to remove dirt rather than keeping it suspended in the oil is basically correct. With care and experience the blotting-paper test can give a very useful indication of the state of the oil of an engine. A drop is placed in the centre of a sheet of filter paper (or blotting paper) will spread slowly to give concentric rings of light and dark regions. A new oil gives a translucent, pale yellow spot. A used oil will give a dark central spot, the size and intensity depending on the dirt level of the oil. The effectiveness of the dispersants and detergents can be noted by the distance of the dark spots when compared to that of the clear edge of the base oil. An alternative technique involves the use of High Pressure Liquid or Gel Permeation Chromatography which can separate the polymeric Viscosity Index Improvers, detergents and dispersants from the base oil. These chromatography techniques allow the quantity of polymeric additives to be determined, along with changes in chemical composition or molecular mass. Wear debris and carbon levels present in the used oil, however, cannot be determined by these chromatographic methods as they are large and insoluble in the solvent system.

## 2.9 DETERMINATION OF WATER IN OILS.

The combustion of any hydrocarbon in the presence of oxygen results in the formation of water and carbon dioxide. Most of the water is lost through the exhaust system. Some products of combustion find their way into the crankcase as a result of blowby past the piston rings or through direct absorption by any circulating oil that it may come into contact with. Formulated lubricating oils can take up significant quantities of water vapour and used oils probably even more. The water vapour will almost certainly be associated with the oil additives such as the metallic detergents and the inorganic anti-acid agents. Water vapour will condense in the cold regions of the engine although some of this water may be evaporated if the engine oil temperature is allowed to exceed 100 °C. If the water is allowed to accumulate in an engine due to infrequent oil checks or due to frequent short journeys, especially in cold and humid climates, then the water may extract acids and additives out of the oil and cause corrosion of bearings, cylinder bores and other engine components. The water may also emulsify with the oil to form sludge which may result in poor lubrication and eventual catastrophic failure due to oil ways becoming blocked.

It is essential to determine therefore, the presence of unacceptable levels of water in an oil. If water levels in lubricating engine oils can be monitored regularly, then any harmful buildup of water can be avoided. In addition, if the engine is water cooled, then any coolant leaks from seals and gaskets can be ascertained at the earliest possible time, before the engine breaks down during service.

There are two IP test standards, namely IP 74 and IP 75, for the determination of water in oils. IP 74 is basically a Dean and Stark distillation and IP 75 is based on a centrifuge method. Neither of these two test standards are applicable to small samples of oil containing less than 0.5% water. Alternative methods for the determination of water in such cases is given in section 3.3. The Karl-Fisher water determination is the most widely used wet chemical analysis technique. The Karl-Fisher analysis allows water content below the 0.5% level to be determined. The Karl-Fisher analysis requires the rigorous exclusion of atmospheric moisture and employs the use of obnoxious chemicals/solvents. The chemical selectivity of the Karl-Fisher reagent is questionable when applied to used lubricating oils and is reflected by the poor repeatability of results on used oils. These problems of the Karl-Fisher analysis, taken together, cannot offer a satisfactory, simple or reliable route for an automated analysis of water content in used oils.

## **2.10 TOTAL INSOLUBLE MATTER IN OILS.**

The combustion of any hydrocarbon in the presence of oxygen results in the formation of water, carbon dioxide and partially oxidised compounds such as aldehydes and nitrogen oxides. In the case of combustion where the amount of hydrocarbon is far in excess to the amount of oxygen available to completely oxidise the hydrocarbon, soot formation is favoured. These products of incomplete combustion enter the lubricating through blowby and accelerate the oxidative degradation of the oil. Also, it is argued that the presence of finely divided wear debris further assists in the degradation of the oil. The lubricating oil in internal combustion engines becomes discoloured with engine operational time. The presence of soot, wear debris and partially oxidised material in the oil eventually changes the oil's physical and chemical characteristics such that it may damage the mechanical integrity of the engine. This would arise due to resinous material of high molecular mass being formed which may become deposited in oil ways and various other parts of the engine thereby causing inadequate lubrication and heat transfer. The presence of resins of high molecular mass may also increase the viscosity thus further impairing the operation of the engine, especially during starting. It is therefore important that the lubricating oil is changed regularly or, better, as soon as it is likely to be a cause of concern.

The state of the oil can be easily ascertained by noting its viscosity, colour and smell. These subjective tests may be difficult for the untrained person and may be a health risk if done frequently. Therefore, an easy physical test needs to be carried out. Many types of oil viscosity checks are in use, including a simple timed-flow comparator between a new and a used oil. The quality of "smell" between oils of varying stages of degradation is subjective and is unlikely to be used, except by those who have a professional "nose" for it and its practice cannot be recommended for health reasons. The blackness of an oil can be determined by various instrumental techniques based on light radiation and absorption characteristics of the oil. Alternative tests such as the blotter spot test and the IP 316 (ASTM D-892) "pentane insolubles" test are used but both methods suffer from drawbacks. The main drawbacks of the "pentane insoluble" test are:

1. It requires the use of pentane-oil mixtures to be centrifuged at high speeds with some risk of explosion,
2. Repeatability of the test arising from dilution errors and the problems of interpretation of the results, and
3. Difficulty to automate.

In the case of the oil-blotter spot test, the main drawbacks are its repeatability, time taken to develop a reasonably sized spot and its interpretation in the degree of

blackness of dark used oils.

Therefore, new approaches to used lubricating oil analyses are required, as are explained in the next chapter.

## CHAPTER 3.

### 3. DEVELOPMENT OF NEW OIL ANALYSIS TECHNIQUES.

Many of the accepted lubricant analysis and test methods, as designated by the Institute of Petroleum and its North American counterpart, the ASTM, originated from engineers who had little in-depth understanding about the physical and chemical nature of the test procedures they developed. These out-of-date test methods have become industrial standards even though some of the knowledge, equipment and working practices are no longer viable. When these standards were proposed, it was likely that testing of large numbers of samples was not considered.

In any case, these standard test methods are long, expensive and cannot be automated at reasonable cost. There has been much development in recent years to understand the basic chemistry of formulated lubricating oils, friction and wear. The following sections discuss details of new methods that have been extensively developed to carry out automated analysis with a throughput of at least 15 samples per hour.

#### 3.1 TOTAL BASE NUMBER.

##### 3.1.1 Methods of TBN Determination.

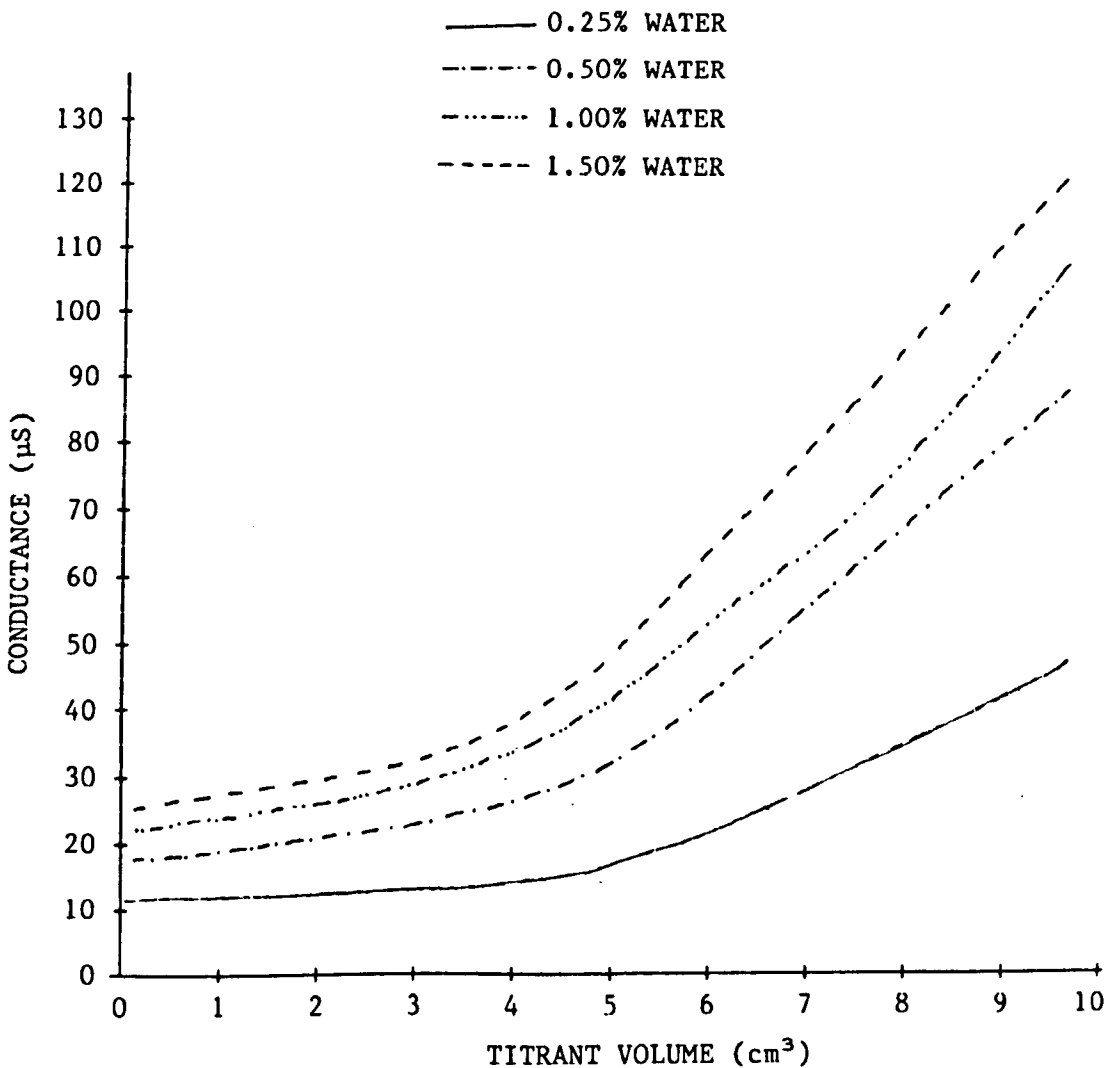
The history, chemistry and techniques available for Total Base Number (TBN) determination has been described in Chapter 2, section 2.1. The chemistry of acid-base titrations in aqueous solution is well defined and clearly understood. Water is a peculiar solvent which imposes limits and constraints that are all too often overlooked. The chemistry of acid-base titrations in non-aqueous solvent systems can be understood only if it is not compared with that which takes place in aqueous solution. The choices of solvent for the non-aqueous TBN determinations are complex mixtures and the composition of formulated lubricating oil complicates effects them even further, in addition to the changed chemical composition and characteristics of used oils.

Given that acid-base titrations, in whatever solvent system, are basically one of chemical equilibrium between the various species involved, the only factor that needs to be addressed is that of measuring the species under investigation, without altering the status quo in the process. The choice to find a better method for determining TBN was simplified by deciding that the same solvent, titrant and their quantities were to be used as in the accepted standard IP methods. Thus, the basic chemistry of any new test method would remain unchanged from that using the accepted methods, the method of detection was to be investigated.

### 3.1.2 Conductimetric TBN Determinations.

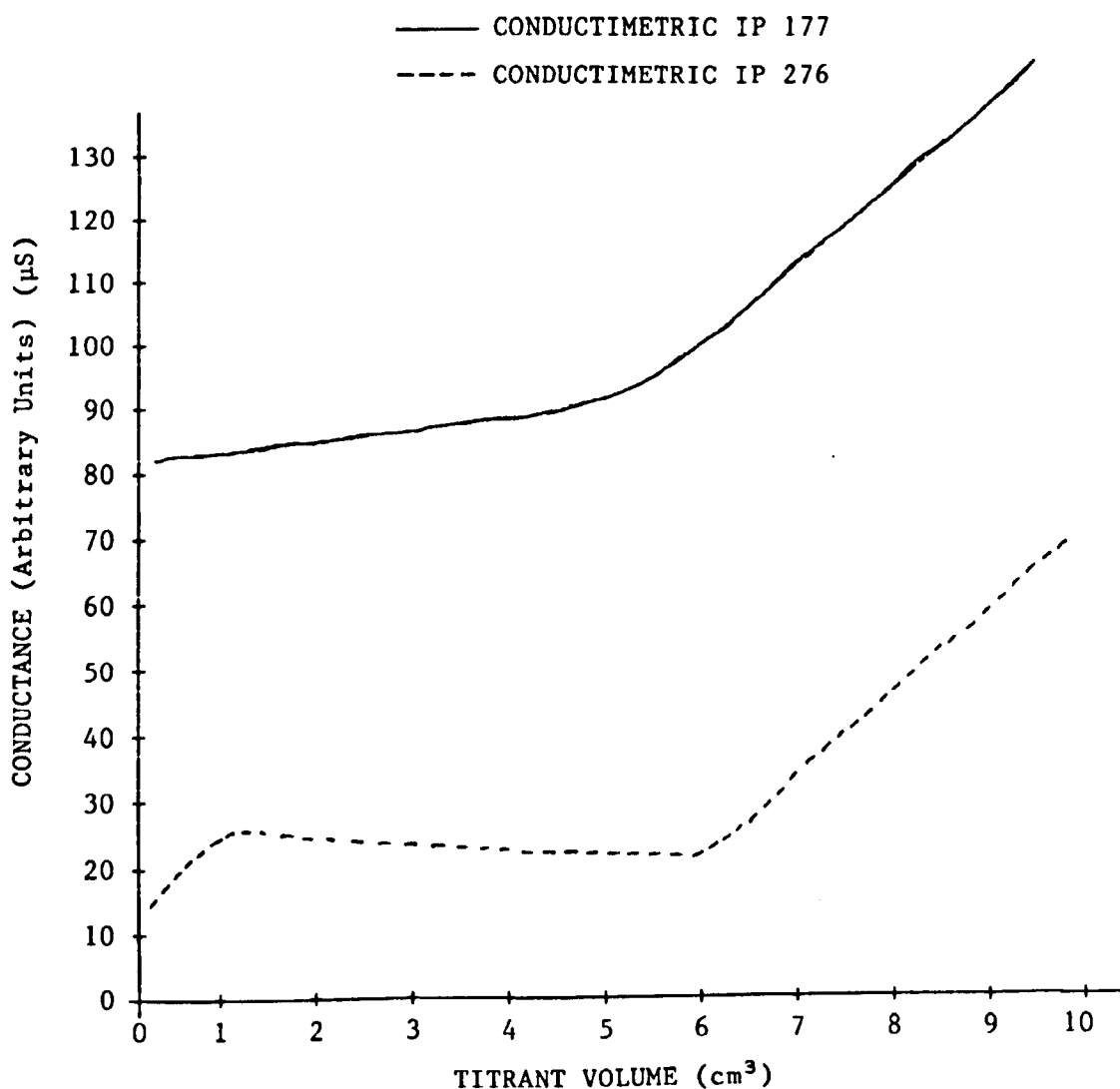
Because of the problems experienced by the standard IP 177 and IP 276 TBN test procedures referred to in section 2.1, it is preferable that the TBN determination is carried-out for new, used and contaminated oils, using a single technique which gives the same quality of end-point characteristics for any oil sample. Such a technique would lend itself to automation, which then allows the problems of repeatability, reproducibility, sample size, costs and analysis time to be addressed. With these objectives in mind, alternative TBN test techniques were reviewed. The conductimetric titration technique was chosen for its greater accuracy, simplicity, ease of analysis, electrode robustness, compatibility with the standard test methods using the same chemistry and most importantly, giving results comparable to those obtained by the standard techniques, without having to use back-titrations or buffers.

**FIGURE 13.** EFFECT OF WATER ON CONDUCTIMETRIC TITRATION CURVES.



The conductimetric technique was developed from the initial work of Pawlak [27] on the water sensitivity of the IP 177 solvent system, and extensively developed during this work at Leicester Polytechnic for TBN determination using both the IP 177 and the IP 276 solvent systems. The work by Pawlak on the addition of water, from 0.5% to 3.0% vol/vol, to improve the sensitivity of the IP 177 conductimetric titration was repeated. Some preliminary work carried out with gradually increasing the water content, from 0.5% to 3.0%, of the toluene/propan-2-ol/water system, showed no effect on the end-point, but confirmed the increase in slope of the intersecting lines first observed by Pawlak, Figure 13. Pawlak does not report, however, on the application of the conductimetric technique with the IP 276 solvent system, which requires conductance one order of magnitude lower than that observed in the IP 177 solvent system.

FIGURE 14. TYPICAL CONDUCTIMETRIC TITRATION CURVES.





The conductimetric method of TBN determination used in this work has the same solvent systems and reactants as used in the IP 177 and was found to be applicable to the IP 276 standard test methods. The replacement of the potentiometric method by the conductimetric method gives a much better defined end-point and so gives better accuracy than the standard IP methods, Figure 14. The conductimetric titration curve is composed of two intersecting straight lines, the intersection of which represents the end-point, instead of a sigmoidal curve obtained using the potentiometric method. The quality of the end-point, when determined conductimetrically, does not degrade with used or severely abused lubricating oils. It is not necessary to carry out a conductimetric back-titration when analysing used oil samples and satisfactory end-points can be obtained for oil samples containing water.

The advantage of the conductimetric method over the potentiometric method is that the shape of the titration curve is the same for new, used, or water contaminated oil samples. In particular, the conductimetric TBN method gives excellent end-points for those severely abused, used oils which would require TBN determination by the back-titration technique.

### 3.1.3 Comparison of Different TBN Test Methods.

A comparison of the results obtained from this work for the potentiometric and conductimetric methods, using both IP 177 and IP 276 solvent systems, with authentic oil samples, is given in Table 15.

The new and used oil samples were obtained from various sources in addition to a military reference oil, marine oils and British Rail diesel locomotive oils for this work, so as to cover a large, but representative, range of TBN for comparison. The data given is a random subset of an extensive collection of determinations.

The conductimetric titrations were carried out manually using a self-balancing a.c. conductance bridge, a conductivity cell consisting of a pair of bright platinum plates, a finely graduated burette, and a magnetic stirrer. The IP 177 conductimetric titration has a 0.1 to 20  $\mu$ S conductance range whereas the IP 276 system has a range of 0.01 to 2  $\mu$ S. For the IP 177 system, conductance increases slowly and linearly up until the titration end-point after which the conductance rises rapidly and (almost) linearly. With the IP 276 system, the conductance initially increases sharply up to a plateau which only increases sharply again after the titration end-point.

The results in Table 15 below, show disparities between the conductimetric IP 177 results and both the potentiometric and conductimetric IP 276 results for the same

oil. The IP 177 results are about 60% of that for the IP 276 results. It is generally accepted that the IP 276 TBN results are higher than that of the corresponding IP 177 results; the difference can vary from near zero for new oils to over 50% for used oils. This difference between the TBN values by the two different methods has been the subject of investigation by other workers, for example Sharma, *et. al.* [34]. A likely explanation may lie in the fact that the different solvents cover different "pH" ranges in essentially non-aqueous media, as explained previously.

**TABLE 15.** COMPARISON OF TBN VALUES DETERMINED BY DIFFERENT METHODS.

IP 276 Potentiometric	IP 276 Conductimetric	IP 177 Conductimetric
8.3	8.9	7.5
6.5	6.8	4.7
8.4	9.5	6.8
29.6	28.4	22.4
29.8	30.8	25.3
30.1	30.8	24.3
27.0	27.5	16.0
8.3	8.5	5.5
8.5	8.0	4.8
8.1	8.0	5.5

The conductimetric and potentiometric IP 276 results are almost the same and certainly are well within the error band of 6% stipulated in the IP 276 test procedure for new oils having TBN up to 59.9 mg KOH/g. The results obtained above were repeatable and promising enough for the method to be semi-automated or fully automated.

A succinct comparison of the potentiometric and conductimetric TBN methods is given in Table 16, below. The table above can be applied equally to either the IP 177 or IP 276 systems. The solvent and titration systems between the potentiometric and the conductimetric systems is the same. The titration chemistry remains unchanged and, therefore, whatever significance the users attach to the TBN value will still hold good, provided that the difference in TBN values between the two techniques is minimal. The reference and calomel electrode system employed in the potentiometric technique in addition to having a short life due to electrolyte contamination and leakage, must be cleaned, maintained, tested and meticulously prepared at all times.

The conductance electrodes (a pair of small platinum spades, 10mm squares) require no preparation or maintenance and due to the properties of platinum can be cleaned

by firing or washing. The potentiometric TBN methods work best with large amounts of sample (20 g maximum) but, in so doing, overcome any problem due to non-representative samples for analysis. However, in some applications, such as top-ring zone oil sampling, only milligrammes of sample may be used without significantly affecting the test viability.

The conductimetric technique with its better accuracy is capable of analysing milligrammes of sample as the electrodes and cell can be miniaturised in proportion to give the same magnitude in conductance readings for bigger apparatus. The use of smaller sample sizes means a saving on expensive solvents and the additional problems of hazardous waste disposal.

The a.c. conductance measured does not perturb the titration medium and the response is extremely rapid, whereas, the potentiometric measurement is limited by the slowness of equilibration at the many interfaces present. The potentiometric technique with its drawbacks of time, back-titrations, buffers, blank titrations and the other above mentioned reasons, cannot compete with those characteristics offered by the conductimetric technique which make the latter the superior choice for automation.

The next step was to determine the reproducibility of the conductimetric TBN technique. The more difficult IP 276 method was chosen for the reproducibility study as it requires lower conductance measurement and in the difficulty of interpretation of the end-point from the complex titration curve. The reproducibility study involved six (academic, commercial, government and railway) laboratories familiar with the standard TBN measurements all of which were given the same oil samples and a copy of the conductimetric TBN test method. Eleven oil samples, covering a wide range of different oils and TBN range, were supplied to each of the laboratories involved in the correlation study. Many of these laboratories chose to test their own standard TBN samples by the new TBN method as well. In most cases, it was the first time that the conductimetric TBN method had been used.

**TABLE 16. COMPARISON OF METHODS FOR TBN DETERMINATION.**

	Conductimetric	Potentiometric
Titration Type	Non-aqueous	Non-aqueous
Electrodes	Platinum Easily cleaned	Calomel. Requires regular replacement
Solvent	IP 177 or IP 276 Solvents	IP 177 or IP 276 Solvents
Titrant	IP titrant	IP titrant
Sample Size	0.1 - 1.0 g	10 g
Electrode Equilibrium Time	10 seconds	5 minutes
Time per Sample	3 minutes	25 minutes
Repeatability	Excellent	Poor
Blank Titration	Not needed	Required
Buffer	Not needed	Required
Other Factors	Savings on solvents	Requires large amounts of solvent
Waste disposal	Smaller amount	Large amount
Applicability	New, used and contaminated oils.	New oils only. Does not work well for used oils

The apparatus used by each of the laboratories were different and probably no two apparatus were the same. The personnel who carried out the new TBN analysis were given no formal training, induction or instruction other than the method to be used (given in Appendix A). All the analysis were carried out manually. Each laboratory calculated their own end-point (and hence the TBN value) using the guidelines supplied with the conductimetric TBN test method provided. The results of this correlation exercise are given in Table 17.

The essential features of the results of this correlation exercise are:-

1. The excellent agreement between the results from the IP 276 potentiometric method and the new conductimetric method using the same IP solvents and titrant. One of the potentiometric results exceeded the 15% used oil reproducibility limit whereas none of the conductimetric results did so.
2. The reproducibility of the conductimetric method shows no significant differences for new or used lubricating oils throughout the TBN range studied.

3. All the results for the conductimetric method were obtained using the forward titration only, whereas some of the potentiometric results had to be obtained using the back-titration.

A limited number of results were obtained for the reproducibility of the conductimetric IP 177 TBN test method. These results are summarised in Table 18. The essential features of the results of this exercise are similar to that of the IP 276 reproducibility investigation. The point of particular interest is that two of the oils showed no inflection (N.I.) when tested by the standard potentiometric method, whereas the three participating laboratories each successfully obtained satisfactory results for the same oil.

Following the successful manual conductimetric TBN reproducibility exercise an automated system was developed and assembled in order to miniaturise the system and to make the task of a repeatability exercise less daunting. The automation was carried out in stages and the study was carried out with a semi-automated, computer controlled system.

The semi-automation of the conductimetric TBN (IP 177 or IP 276) determination consisted of an automatic ranging, self-balancing conductance bridge. The analogue output from this conductance bridge was read by a Commodore 64 Microcomputer which reads the conductivity data via a Digital Voltmeter (A/D converter). A piston burette, driven by a stepper motor, is controlled by the Commodore 64 Microcomputer which can add discrete amounts of titrant with microlitres precision. A mass of oil (0.5 - 1.0 g) is placed in a tall reaction flask to which (30 cm<sup>3</sup>) of solvent mixture is added. The computer adds the titrant from the digital burette into a reaction flask containing a known mass of oil and the TBN solvent mixture. The oil-solvent-titrant mixture is stirred using a magnetic stirrer with a Teflon-coated follower. A computer programme (Appendix B) was written to ask for the mass of oil, titrant concentration and aliquot size before it measures the initial conductance reading of the oil-solvent mixture, then adding the first quantity of titrant and allowing the mixture to equilibrate for 30 seconds before measuring the conductance again. The titrant addition and conductance measurement was repeated fifteen to thirty times depending on the mass of oil used, the titrant aliquot size and the TBN of the oil. The schematic flow chart of the semi-automated conductimetric TBN analysis process is shown in Figure 15.

TABLE 17. SUMMARY OF RESULTS FOR MANUAL CONDUCTIMETRIC AND POTENTIOMETRIC TITRATIONS OF TOTAL BASE NUMBER USING THE IP 276 SOLVENTS AND TITRANT.

SAMPLE NUMBER	SAMPLE ORIGIN	COMMENTS	LEICESTER POLYTECH.	BRITISH RAIL	ESSO	SHELL	MoD	GDANSK
1	MoD ER5D 15W/30	New Cond. Pot.	5.8	5.8 5.8	5.4 5.4	5.2 5.3	5.5 6.0	6.0
2	MoD ER5D 15W/30	100 Hr Cond. Pot.	6.4	6.5 6.3	6.4 5.5	5.7 5.5	5.7 6.3	6.5
3	MoD ER5D 15W/30	250 Hr Cond. Pot.	6.7	6.7 6.6	6.7 5.6	6.2 5.6	6.3 6.0	7.0
4	BR 27/ 20264 15W/40	New Cond. Pot.	9.2	9.5 9.3	8.9 9.0	8.6 8.9	8.9 9.5	9.2
5	BR 27/ 20450 40	New Cond. Pot.	10.0	10.2 10.1	9.5 9.7	9.5 9.6	9.9 9.9	10.2
6	BR HST 40	Used Cond. Pot.	9.2	9.1 9.3	9.0 8.7	8.3 8.7	8.3 8.7	9.3
7	BR TBN Pot.	Used Cond.	9.5	10.5 10.5	10.7 10.1	10.3 10.0	10.8 9.8	10.4
8	BR St. Anselm	New Cond. Pot.	37.9	37.9 37.5	37.4 36.9	37.2 37.0	36.1 37.3	38.4
9	BR St. Anselm	Used Cond. Pot.	28.6	29.5 27.8	29.3 28.4	29.1 28.3	28.5 28.9	28.8
10	BR Hengist	Used Cond. Pot.	18.7	18.3 18.7	19.3 22.0	18.7 19.2	19.1 22.0	20.3
11	BR HST 15W40	Used Cond. Pot.	8.2	7.8 7.9	8.3 7.0	8.7 7.4	8.1 8.2	8.3

**TABLE 18. SUMMARY OF RESULTS FOR MANUAL CONDUCTIMETRIC AND POTENTIOMETRIC TITRATIONS OF TOTAL BASE NUMBER USING THE IP 177 SOLVENTS AND TITRANT.**

SAMPLE NUMBER	SAMPLE ORIGIN	COMMENTS	LEIC. POLY. Conduct.	GDANSK Conduct.	SHELL Conduct.	SHELL Potent.
1	MoD ER5D 15W/30	New	5.1	4.9	5.8	5.1
2	MoD ER5D 15W/30	100 Hr	5.2	5.5	4.9	3.8
3	MoD ER5D 15W/30	250 Hr	5.1	5.5	5.1	4.0
4	BR 20264 15W/40	New	8.9	8.3	9.3	8.9
5	BR 20450 40	New	9.7	8.6	9.5	9.1
6	BR HST 40	Used	7.2	7.9	7.3	6.1
7	BR TBN	Used	8.2	8.6	8.4	8.4
8	BR St. Anselm	New	36.0	36.7	35.3	36.0
9	BR St. Anselm	Used	20.0	25.8	22.0	No Inflection
10	BR Hengist	Used	13.5	18.0	15.3	No Inflection
11	BR HST 15W/40	Used	4.9	6.8	5.4	4.7

The conductivity and volume of titrant added data can be plotted on screen or printer. The TBN is calculated by the computer after it has determined the end-point by calculating the intersection of two best fitted lines to the titration curve.

The results of the semi-automated repeatability study is summarised in Table 19 for the IP 177 method and Table 20 for the IP 276 method. The oils used for this study were taken to cover a range of TBN of new and used oils. The same oil samples were used for both the IP 177 and IP 276 conductimetric TBN repeatability study. In both

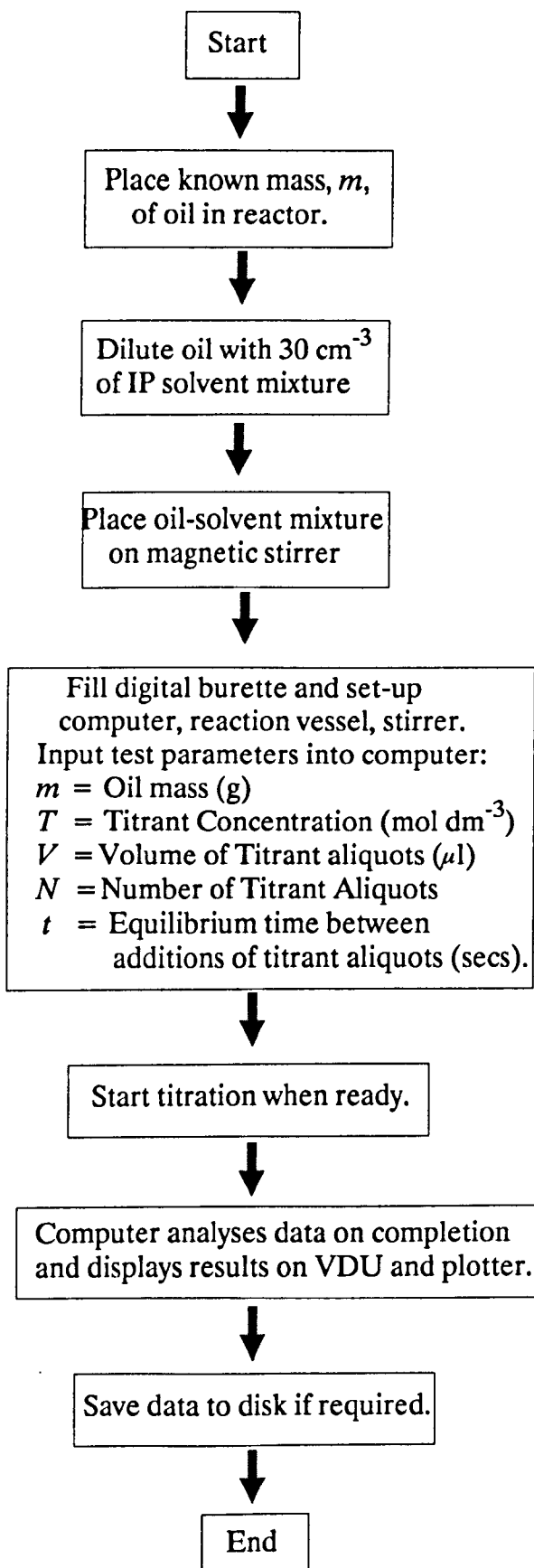
studies the repeatability of the results are excellent as noted by the small standard deviations based on ten analysis for each oil using both methods. Any errors due to inconsistent sample quality and mass measurement were reduced by mixing the oil on a rotary stirrer and careful weighing on an accurate balance.

**TABLE 19.** IP 177 CONDUCTIMETRIC TBN REPEATABILITY STUDY.

SAMPLE NUMBER	NEW LOW ER5D	NEW HIGH 6095	USED LOW 8281	USED MEDIUM 3202	USED HIGH 6481
1	5.34	34.86	1.54	6.25	23.91
2	5.43	34.46	1.52	6.44	24.49
3	5.57	34.53	1.68	6.05	24.06
4	5.56	34.41	1.55	6.77	24.10
5	5.53	34.93	1.51	7.05	24.38
6	5.48	34.78	1.50	6.55	24.30
7	5.38	34.05	1.49	6.80	23.55
8	5.40	34.91	1.60	6.37	23.50
9	5.59	34.10	1.58	6.39	23.88
10	5.46	34.44	1.46	6.66	23.79
Average	5.47	34.53	1.54	6.53	24.00
$\sigma_n$	0.007	0.096	0.004	0.078	0.101



FIGURE 15. SCHEMATIC FLOWCHART FOR THE SEMI-AUTOMATED TBN ANALYSER.



It should be noted that at this early stage of the development of the automated TBN system, that no fine tuning of the measurement and control system was possible in the time available. Such fine tuning of the analysis, control and measurement was to be undertaken on a fully computerised automated system which would have both the degree of resolution and capability to carry out multiple tasks rapidly and simultaneously with other activities.

It can be seen from Table 19 that used oils have lower standard deviations than the corresponding new oils; this is the opposite to that obtained by the potentiometric method. Also, the IP 177 results have a lower standard deviation than that of the IP 276 results for the same samples, see Table 20.

**TABLE 20: IP 276 CONDUCTIMETRIC TBN REPEATABILITY STUDY.**

SAMPLE NUMBER	NEW LOW ER5D	NEW HIGH 6095	USED LOW 8281	USED MEDIUM 3202	USED HIGH 6481
1	6.14	38.55	4.03	9.01	26.09
2	7.14	38.73	4.34	8.70	25.55
3	5.86	38.79	4.53	8.75	26.29
4	6.59	40.00	4.05	8.91	26.46
5	7.45	40.39	4.56	9.21	26.29
6	7.24	40.15	4.97	9.00	26.05
7	7.41	39.85	4.29	8.67	26.78
8	6.74	39.80	4.51	8.94	26.70
9	7.14	39.20	4.43	9.74	26.62
10	6.92	39.69	4.31	8.75	26.51
Average	6.86	39.52	4.40	8.97	26.33
$\sigma_n$	0.257	0.380	0.066	0.092	0.122
IP 276	6.90	41.30	2.71	8.53	29.90

### 3.1.4 Fully Automated Conductimetric TBN analyser.

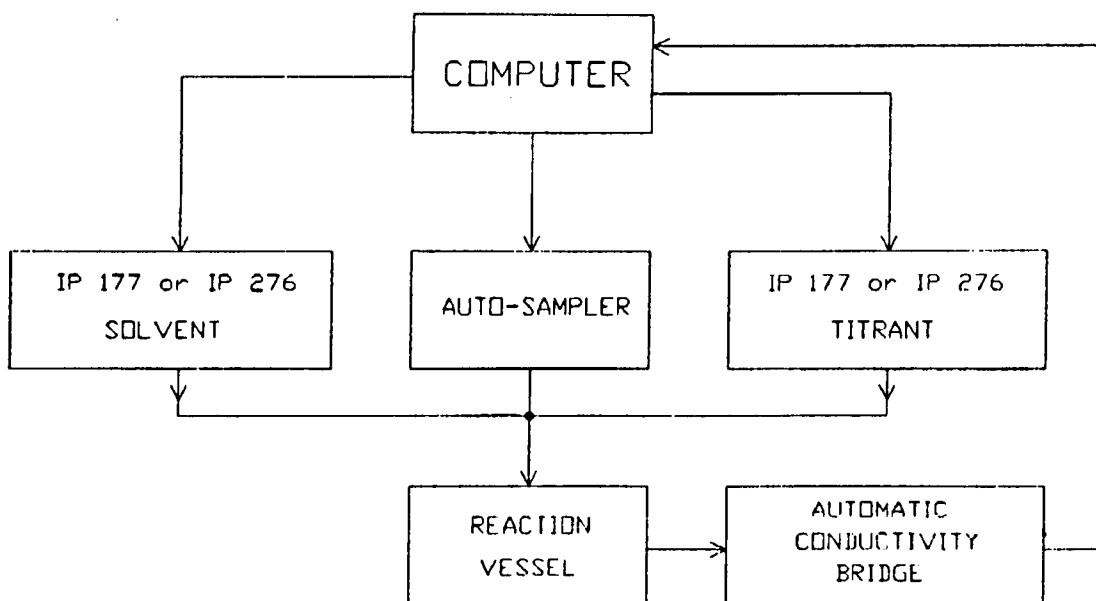
The major aim was to develop an automated system for the analysis of TBN of any oil. This is only possible with the technique of conductimetric TBN analysis as was shown by the excellent results obtained by both the reproducibility and repeatability exercises discussed above. In addition to the processes developed in the semi-automated method, a fully automated system requires the following criteria:-

1. Using the smallest number of components
2. Using oil and solvent compatible materials
3. Sampling oils of various viscosities, from a carousel
4. Presenting a known mass of sample to a titration vessel
5. Dilution with a fixed amount of solvent
6. Thorough mixing of sample, solvent and titrant
7. Thorough cleaning and drying of reaction vessels and associated service tubes before the next sample analysis
8. Titration with acid to an end-point and beyond using a stepper motor driven burette
9. Following the progress of the titration with a self-ranging, continuously balancing conductance bridge
10. Calculating the TBN value from the conductance - titrant volume data for each sample
11. All of the above functions to be failsafe against loss of power, spillage and to be controlled, checked and monitored using a microcomputer
12. Data to be stored and sent to a central or other computers.

Of the above listed requirements, the major problems encountered were of material compatibility, cleaning of tubes and metering of solvents.

An initial systems analysis showed the sequence (Figure 16) to be:-

FIGURE 16. SCHEMATIC LAYOUT FOR THE AUTOMATED CONDUCTIMETRIC DETERMINATION OF TBN.



#### 3.1.4.1 Material compatibility.

It was discovered that chlorobenzene attacked and caused swelling of most rubbers whereas the glacial acetic acid would attack those rubbers and plastics that were resistant to chlorobenzene. This incompatibility meant that peristaltic metering pumps could not be used for the IP 276 solvents. Teflon and glass were the only materials to effectively withstand the IP 276 solvents and titrants.

#### 3.1.4.2 Cleaning the system.

Having chosen teflon and glass, the cleaning problem was overcome by the use of a venturi system which created small, air bubbles at regular intervals, in a stream of titrant solvent mixture. This combined action of air and solvent "pulses" in the small bore teflon tubes, effectively and efficiently removed all traces of contamination. This tube washing is akin to a type of solvent extraction involving many thousands of individual extractions.

#### 3.1.4.3 Metering of solvents.

In order to ensure a rapid and accurate metering of solvents, a regulated dry, air supply was found to offer the best and cheapest answer, and offering the added bonus of 'blow-drying' the tubes and titration vessel when required.

The overall scheme of the above fully automated TBN analysis system is shown in Figure 17. The sampling head and carousel movements are controlled and checked by the computer.

FIGURE 17. AUTOMATED TBN ANALYSER SYSTEM FLOWCHART.

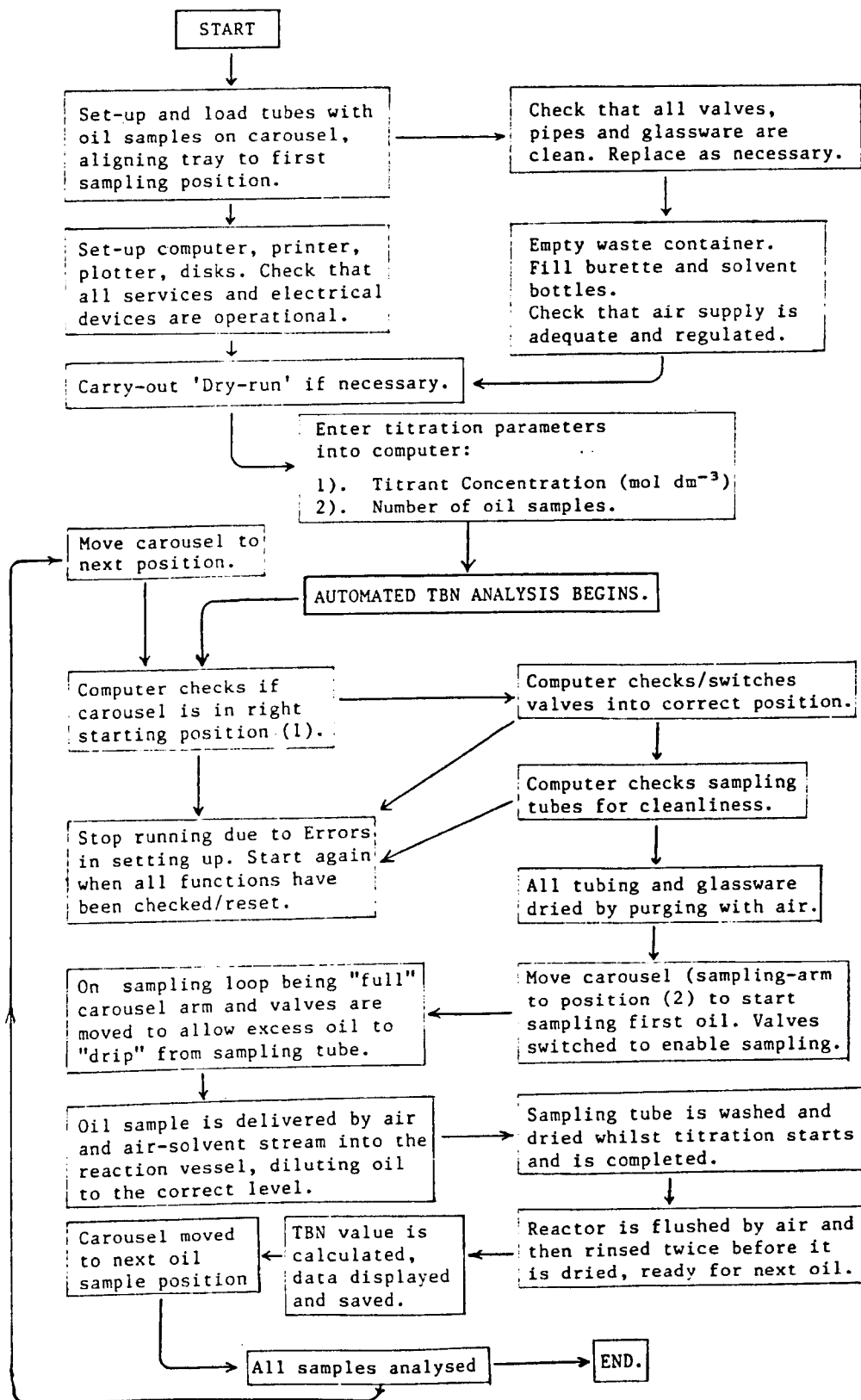


FIGURE 18: TYPICAL IP 177 CONDUCTIMETRIC TITRATION CURVE END POINT DETERMINATION.

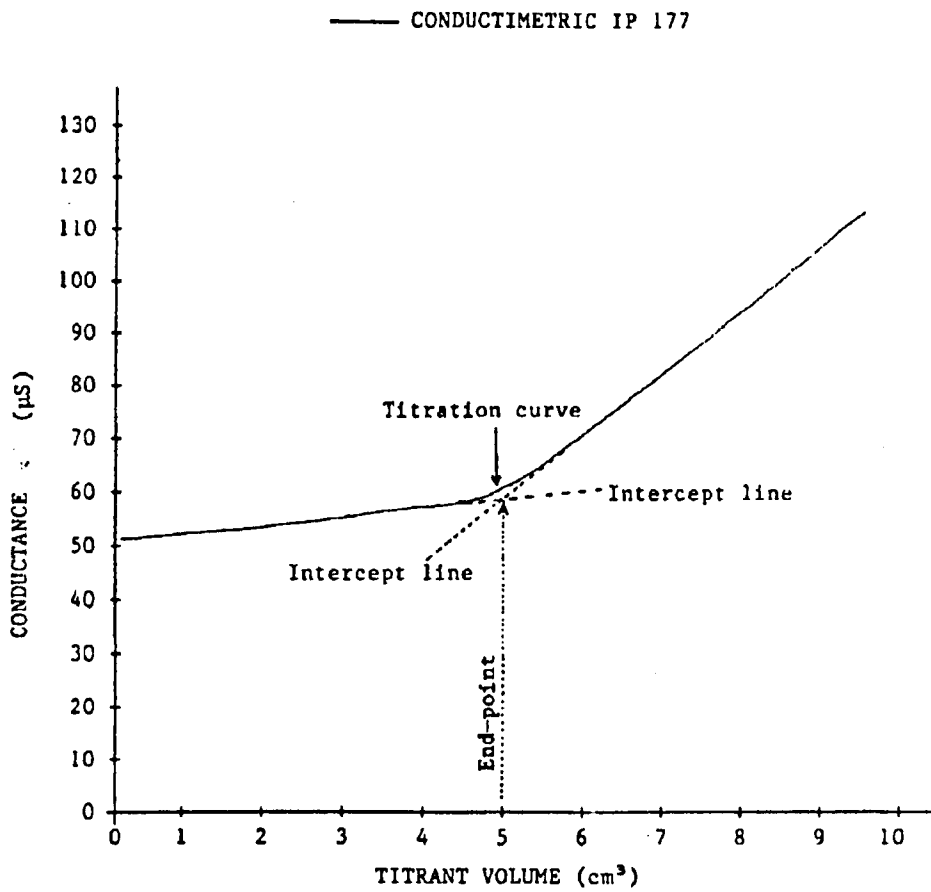
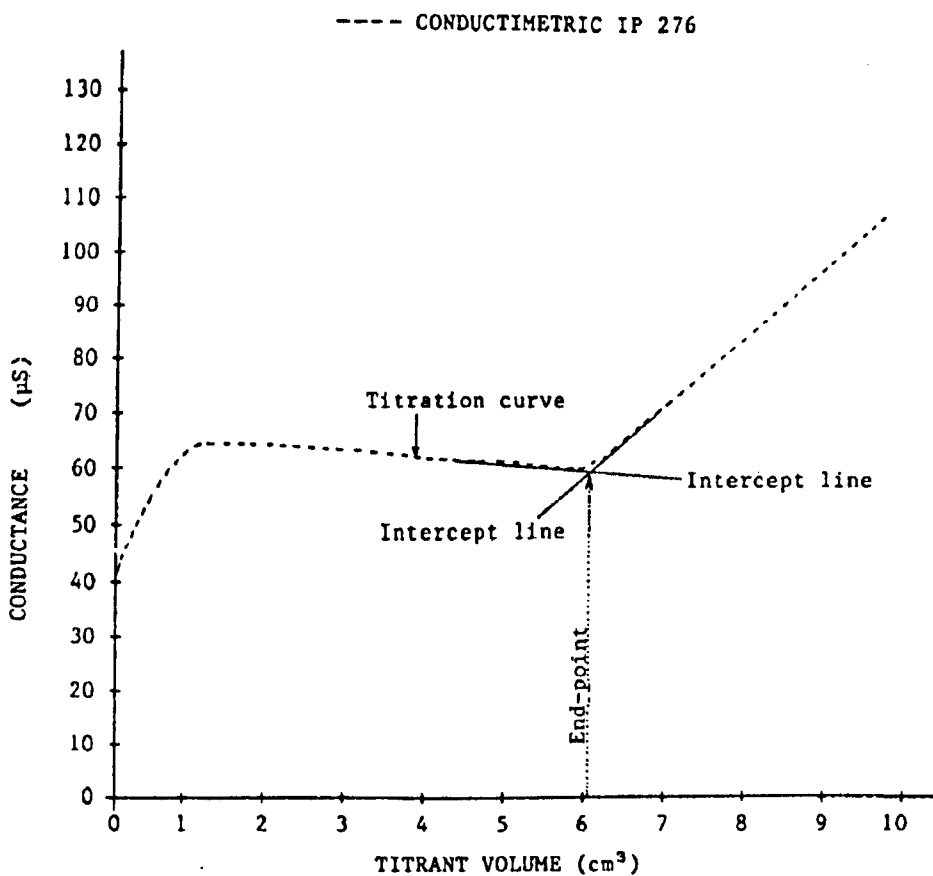


FIGURE 19: TYPICAL IP 276 CONDUCTIMETRIC TITRATION CURVE END POINT DETERMINATION.



#### 3.1.4.4 Oil sampling, delivery and dilution.

Oil is drawn into a sampling loop of known volume by a small vacuum pump. When the sampling loop is detected as being full by a photocell, the sampling valves are switched and the oil sample is flushed into the titration vessel using compressed air. The remaining oil in the sampling loop is washed through with a stream of titration solvent mixture containing deliberately entrained air bubbles, to ensure efficient scavenging of any remaining oil in the sampling loop. The microcomputer precisely meters the volume of titration solvent mixture used to transfer the oil sample to the reaction vessel. The final mixture concentrations delivered correspond exactly with the respective standard IP methods. However, the volumes used are much smaller and entirely satisfactory results are obtained with 8% of the IP recommended quantities, that is, 10 cm<sup>3</sup> instead of 120 cm<sup>3</sup>.

#### 3.1.4.5 TBN Titration.

The titration may be conducted in one of two ways. It may be performed so that a fixed number of constant aliquots of titrant are to be added, in the knowledge that such a total volume is more than sufficient to complete the titration. This is the preferred mode of operation when only one range of oils (or TBN) are to be analysed of known maximum TBN. Alternatively, the titration is carried out until the final conductance of the solution rises to a preset value; that value being set beyond the maximum end-point that would be encountered.

#### 3.1.4.6 End of titration system cleaning.

When the titration has been completed, the reaction vessel is emptied by applying low air pressure to cause the contents to siphon into a waste tank. The cell has a small diameter air vent to allow for variations in liquid volume but the air flow rate through this vent is insufficient to equilibrate pressure when the pressure pulse is applied to commence the siphon. The vessel is then washed twice by filling with 1,1,1-trichloroethane, stirring vigorously and siphoning as before. The reaction vessel is then purged with dry air to dry it before the next sample is to be analysed.

### 3.1.4.7 TBN determination

The conductance/titrant volume for the fixed volume of oil (if the density is known, then a known oil mass) is first analysed to roughly locate the end-point by a simple difference method. This is essentially looking for large positive difference between consecutive readings following a series of small (negative, zero or positive) differences. Having obtained an initial rough estimate of the end-point position, seven points either side of the selected point are best-fitted to either a straight line (IP 177) or a quadratic equation (IP 276) and their intersection is taken as the final end-point, see Figures 18 and 19, respectively.

The cycle time between oil TBN analysis is of the order of four minutes for the IP 276 conductimetric TBN, enabling a total throughput of approximately fifteen samples per hour. The cycle time between the oil analysis for the IP 177 conductimetric TBN is of the order of twelve samples per hour due to its longer equilibration times. The complete listing of the computer programme for the fully automated conductimetric TBN method is given in Appendix C.

The fully automated instrument layout is shown in Figure 20. The instrument was assessed for repeatability using both the IP 177 and IP276 solvent systems for the same eleven oil samples used in the reproducibility exercise and an additional oil as a quality check. The results from these tests are summarised in Table 21 and are given in detail in Table 22 for the IP 177 system and Table 23 for the IP 276 system. The essential features of these results are:-

1. The excellent repeatability, with a standard deviation of about 5% on both new and used oils, which is within the Institute of Petroleum quoted figures on precision (Table 14). It should be noted that only the forward titration is employed in the conductimetric method, whereas, most of these used oils would require a back titration.
2. The results show no significant differences in precision for new or used lubricating oils throughout the TBN range of oils and oil types studied.
3. The conductimetric TBN method has been shown to be superior in versatility, application, performance and cost over the standard IP methods.



**TABLE 21: SUMMARY OF RESULTS FOR AUTOMATIC CONDUCTIMETRIC TITRATION OF TOTAL BASE NUMBER USING IP 177/ IP276 SOLVENTS.**

SAMPLE	IP 177		IP 276	
	MEAN	STD DEV	MEAN	STD DEV
A	9.3	0.30	9.5	0.53
B	6.5	0.21	5.8	0.27
C	5.3	0.31	6.5	0.34
D	5.9	0.20	6.3	0.33
E	9.6	0.26	9.4	0.29
F	10.8	0.31	10.4	0.35
G	7.6	0.21	9.0	0.64
H	9.5	0.24	10.7	0.53
I	38.9	1.14	41.7	0.73
J	23.7	1.31	31.1	1.54
K	16.6	0.81	20.8	0.77
L	5.4	0.20	8.2	0.32

### 3.1.5 TBN Thermal Degradation.

New, formulated lubricating oils contain alkaline additives (e.g. calcium sulphonate, carbonate and hydroxide) that contribute to the Total Base Number. These additives, however, may not account for all of the observed TBN value. The TBN value obtained by the IP 276 method is usually higher than that obtained by the IP 177 method. The difference in TBN values is small for new oils but it progressively increases with the used life of the oil. Hook [28] has obtained different, decreasing, TBN values for the same diesel engine oil using three different acids, namely perchloric, sulphuric and hydrochloric acids, respectively, using either of the two IP solvent systems. Fox, Pawlak, Fox and Picken [27] obtained TBN values for some selected products such as zinc-dialkyl-dithiophosphate using the IP 276 back-titration and conductimetric methods. This shows that the ZDDP anti-oxidant reacts with the perchloric acid, with hydrogen sulphide being liberated and so contributes to the observed TBN value. Nitrogenous compounds employed as ashless dispersants has also been shown to contribute to the observed TBN value [34]. Some oils have been found to show an increase in the IP 276 TBN value with operating time of the oil.

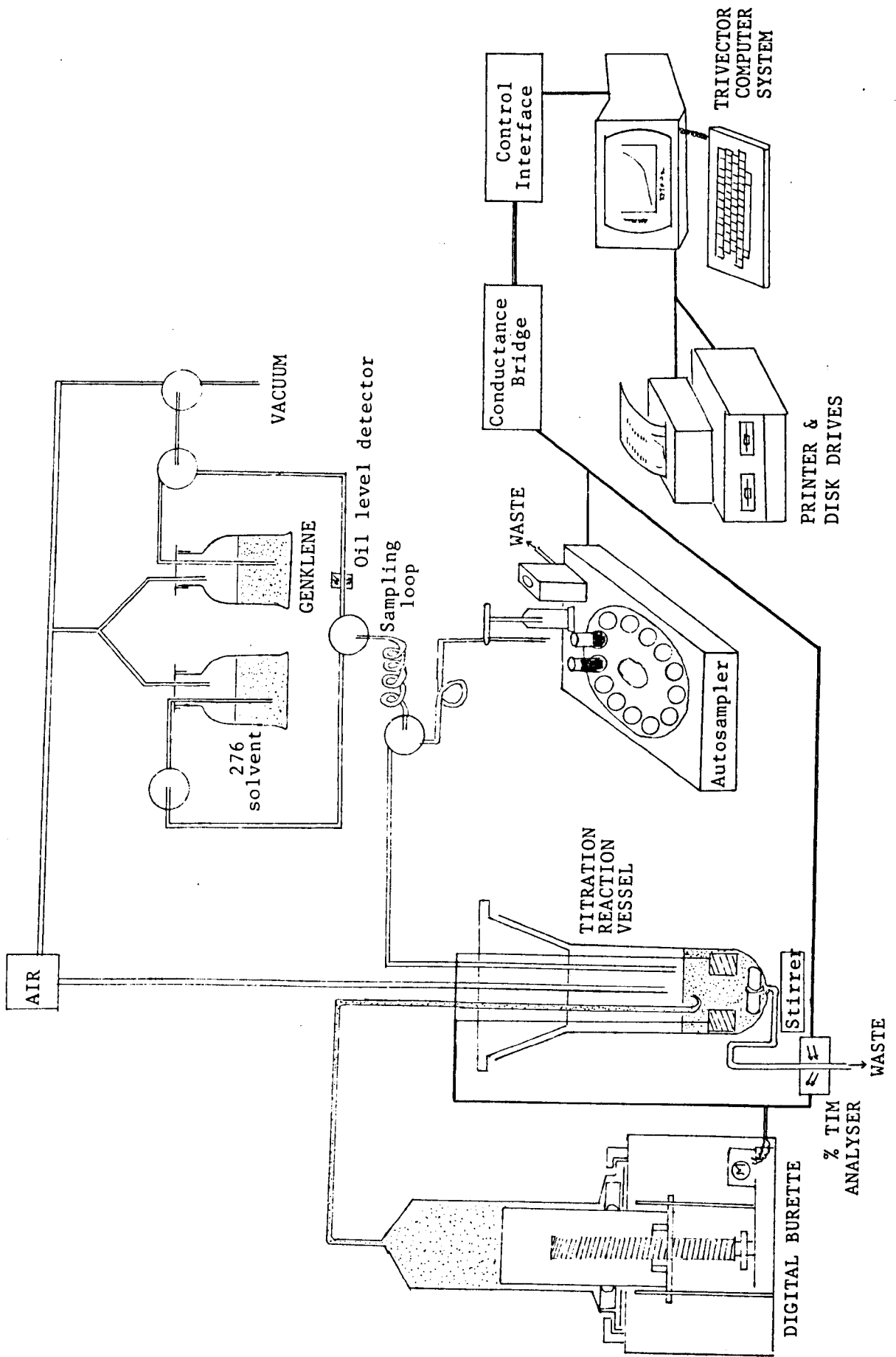
TABLE 22. SUMMARY OF RESULTS FOR THE AUTOMATED CONDUCTIMETRIC TITRATION OF TOTAL BASE NUMBER USING IP 177 SOLVENTS.

A	B	C	D	E	F	G	H	I	J	K	L	
9.7	6.8	5.7	5.7	10.1	11.1	7.7	9.6	38.8	25.2	17.1	5.2	
9.7	6.1	5.1	6.2	9.5	11.0	7.4	9.5	37.5	21.9	17.5	5.7	
9.2	6.7	5.3	5.7	9.1	10.4	7.5	8.7	37.1	22.3	17.7	5.3	
9.6	6.2	5.3	5.8	9.7	10.4	7.5	9.6	38.2	23.3	15.6	5.2	
9.2	6.5	4.8	6.1	9.8	11.3	7.9	9.5	38.6	25.2	18.3	5.6	
9.4	6.2	5.5	5.9	9.8	10.4	7.7	9.3	40.0	24.8	15.6	5.4	
9.4	6.5	5.2	6.1	9.5	10.4	7.2	9.3	40.0	25.1	15.9	5.6	
9.2	6.2	5.0	5.8	9.6	11.1	7.5	9.5	37.5	21.8	15.9	5.3	
8.8	6.4	5.7	5.7	9.2	10.6	7.5	9.6	39.4	22.9	16.7	5.2	
9.1	6.4		5.8	9.6	10.7	7.6	9.6	39.4	23.8	16.8	5.3	
8.8	6.8		5.7	9.5	11.0	7.9	9.5	38.2	24.0	15.9	5.2	
9.6	6.5		6.2	9.7	10.5		9.6	40.7	24.7	16.4	5.7	
9.4	6.5		6.0	9.8	11.1		9.5	40.0	23.5	16.6	5.5	
9.1	6.5				11.0		9.7		25.1	17.1		
9.2	6.5				11.0		9.5		21.8	15.9		
9.3	6.4				10.9		9.6			15.9		
9.7							9.1					
9.5												
9.6												
8.8												
9.3												
9.8												
9.2												
MEAN	9.3	6.5	5.3	5.9	9.6	10.8	7.6	9.5	38.9	23.7	16.6	5.4
STD.DEV	0.30	0.21	0.31	0.20	0.26	0.31	0.21	0.24	1.14	1.31	0.81	0.20
DATA No.	23	16	9	13	13	16	11	17	13	15	16	13

TABLE 23. SUMMARY OF RESULTS FOR THE AUTOMATED CONDUCTIMETRIC TITRATION OF TOTAL BASE NUMBER USING IP 276 SOLVENTS.

A	B	C	D	E	F	G	H	I	J	K	L
9.7	9.3	5.8	6.2	6.2	10.3	8.6	10.2	41.7	31.6	19.9	8.3
9.7	9.5	5.8	6.2	5.8	10.3	7.7	10.9	42.3	30.2	19.6	8.1
9.4	8.7	6.2	6.7	6.3	10.3	8.6	10.4	41.0	27.1	21.3	8.6
8.5	9.7	6.2	6.9	6.2	9.8	8.8	11.2	42.1	28.9	20.8	7.8
8.6	9.6	5.9	6.1	9.2	10.1	7.9	10.3	42.4	29.5	18.8	8.0
9.2	9.5	5.0	6.3	5.8	10.0	7.8	9.6	42.3	30.0	19.3	8.2
8.3	8.9	6.0	5.9	5.7	9.9	8.6	9.5	42.1	32.3	21.5	8.1
8.6	9.5	6.1	6.1	5.5	9.6	8.7	10.7	42.0	31.3	21.2	8.0
9.4	10.7	5.6	7.4	6.3	9.1	9.0	11.2	41.1	29.3	20.8	8.0
9.1	10.2	5.7	6.6	9.2	10.7	8.7	10.0	41.8	30.3	20.0	8.4
9.9	10.4	5.6	6.4	6.5	9.1	8.7	10.1	42.0	28.9	20.9	8.3
9.5	9.1	5.7	6.4	6.3	9.5	9.2	10.4	42.4	32.4	20.2	7.8
9.2	10.1	6.0	6.8	6.7	9.4	8.9	10.8	41.5	32.1	20.2	8.8
9.6	9.8	5.5	6.5	6.5	9.1	9.1	10.6	42.5	31.0	20.5	8.2
8.9	10.0	5.4	6.0	6.9	9.0	9.6	11.0	41.3	31.8	20.9	8.2
8.9	9.9	6.1	6.5	6.6	9.3	10.5	11.1	41.3	30.0	21.1	8.8
9.1	9.8	5.9	6.3	6.2	8.9	10.6	10.9	40.7	33.0	21.7	8.1
9.7	9.9	6.0	7.0	6.0	9.1	10.3	9.5	41.6	32.7	21.6	8.8
9.4	10.0	6.0	6.3	6.2	9.5	10.6	10.8	41.9	32.9	21.2	8.1
9.9	10.6	5.9	6.6	6.2	9.1	10.6	10.9	39.7	31.9	21.8	7.7
9.2	9.7	6.0	6.4	6.6	9.5	11.0	9.7	42.7	32.0	21.3	7.7
9.6	10.2	5.7	6.2	6.3	9.3	10.7	11.2	41.0	31.5	20.5	8.0
9.6	9.8	5.9	6.6	6.5	9.9	9.4	10.5	42.3	33.1	20.8	8.3
9.2	10.0	6.1	6.6	6.4	9.8	11.0	9.4	42.2	32.1	21.7	8.1
10.1	9.8	5.8	6.5	9.8	10.7	9.7	11.4	43.3	30.4	20.9	
9.4	10.2	6.1	6.7	9.6	10.7	10.6	10.9	42.3		21.0	
		5.9	6.2	9.5	10.6	8.8	10.5	41.0			
			6.1	9.8	10.2	8.9		41.7			
			6.8	9.3		9.4		40.7			
			6.7	9.7		8.8		41.4			
			7.2	9.1		8.2					
			6.5	9.3		9.0					
			6.2	9.4		8.9					
						9.2					
MEAN	9.6	5.8	6.5	6.3	9.4	9.1	10.7	41.7	31.1	20.8	8.2
STD.DEV	0.53	0.27	0.34	0.33	0.29	0.35	0.64	0.53	0.73	1.54	0.32
DATA No.	52	27	33	24	33	28	34	30	25	26	24

FIGURE 20. FULLY AUTOMATED CONDUCTOMETRIC TBN AND TIM ANALYSER SYSTEM.



**TABLE 24.** TBN THERMAL STABILITY IN NEW OILS.

Oil	Time	Atmosphere	Result
ER5D	800 hr	Air	Decreases in 23 hrs.
ER5D	100 hr	Nitrogen	No change
LORCO	1000 hr	Nitrogen	IP 276 small change.
ESSO HDX	400 hr	Air	No change
ESSO IL 3030	500 hr	Air	No change
SHELL DZS	500 hr	Air	IP 276 small change
SHELL B40	500 hr	Air	No change

Work by Sharma [34] indicates that the TBN of a new oil rapidly decreases to a lower, stabilised value. An investigation was undertaken to check if certain new oils would show a similar, initial decrease in TBN when heated under nitrogen and air at 140 °C. The effect on TBN due to the addition of a small amount of water to the new oil was also investigated in an attempt to understand the difference in TBN value obtained by the two IP methods. The results for six different oils are given in Table 24.

The results for each of the above tests are given in Figures 21 to 28. Only one oil was found to show a significant decrease in TBN by IP 276 on heating in air and the TBN decreased from 6.6 to 5.1 mg KOH/g in 23 hours and remained at this stabilised value during the remaining time of the 800 hours test. The same oil when heated under nitrogen showed no change in TBN, although the IP 177 TBN value remained constant at 5.7 mg KOH/g and the IP 276 TBN remained higher at a constant 6.6 mg KOH/g. It is difficult to account for the difference in the results obtained without detailed knowledge of the additive pack composition. It is probable that the results obtained in the presence of air was due to the non-alkaline additives being destroyed in some way such that it can no longer contribute to the Total TBN as obtained by IP 276. It can be concluded from this data that the IP 276 TBN is not a true indicator of the alkali reserve present in the oil once it has entered into service in the engine. The addition of water to the oils tested above, did not appear to affect the TBN level. The conclusion that can be drawn from this is that the additive pack is not water sensitive in the new oil or that the degree of mixing achieved in an engine has not been achieved.

FIGURE 21.

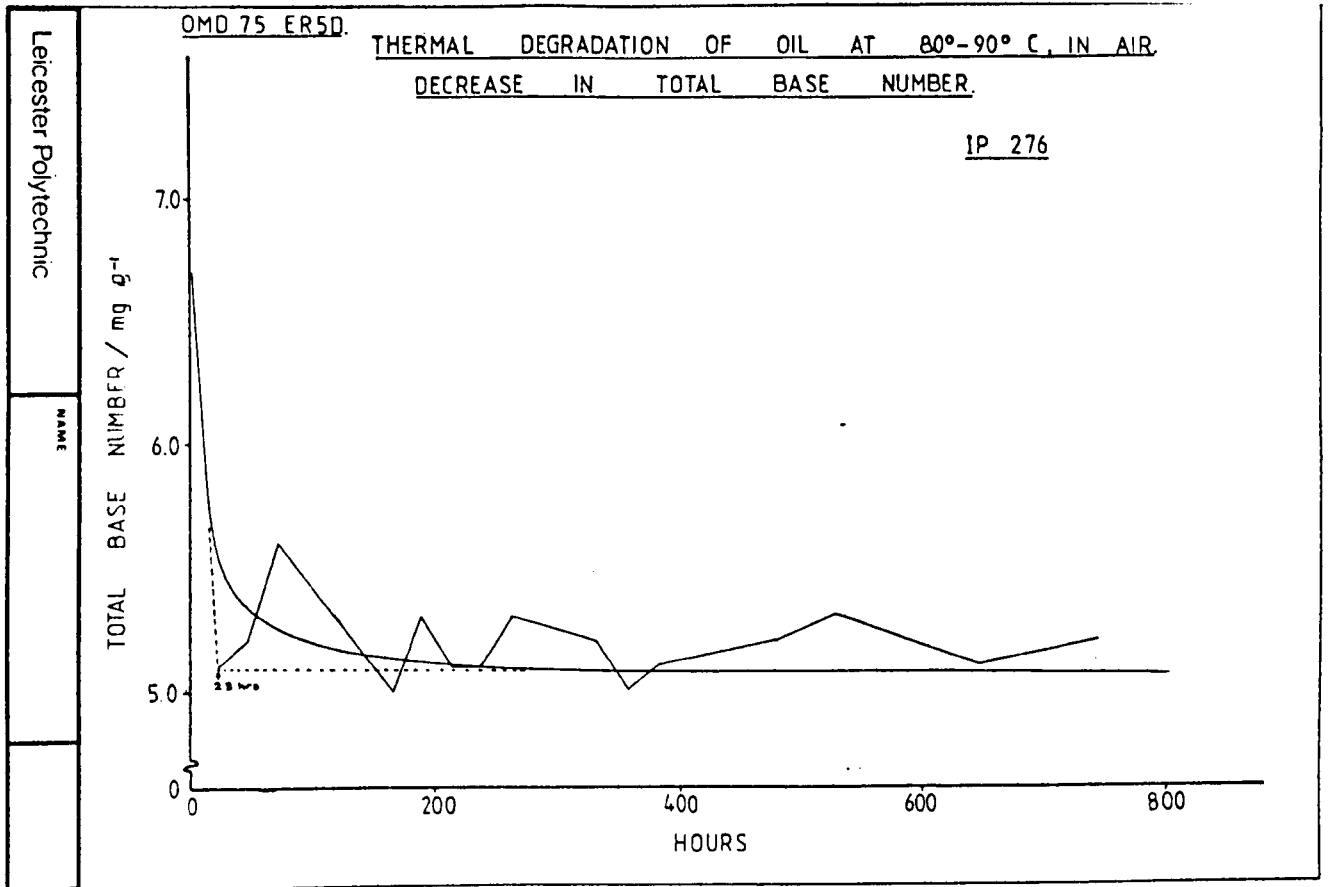


FIGURE 22.

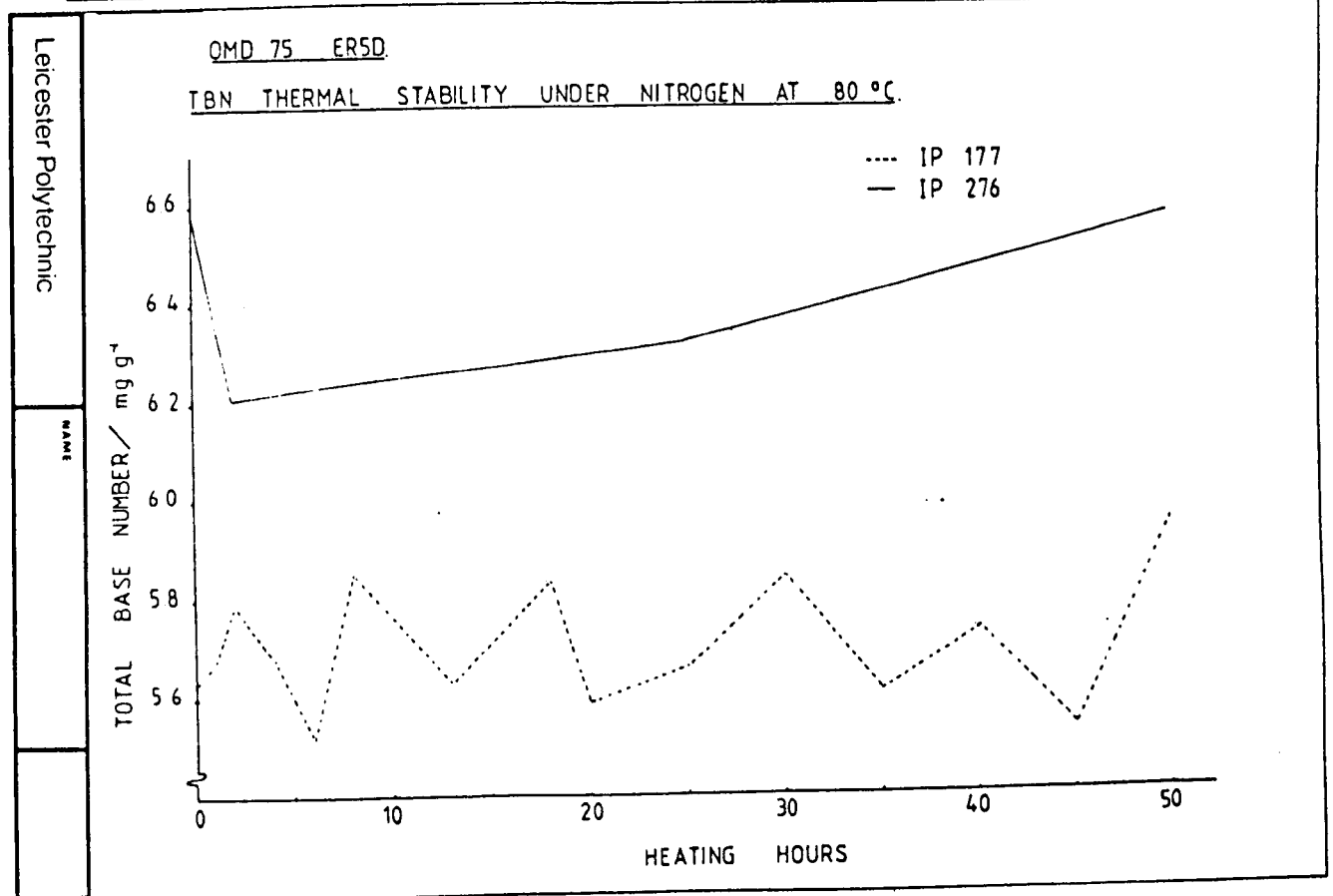


FIGURE 23.

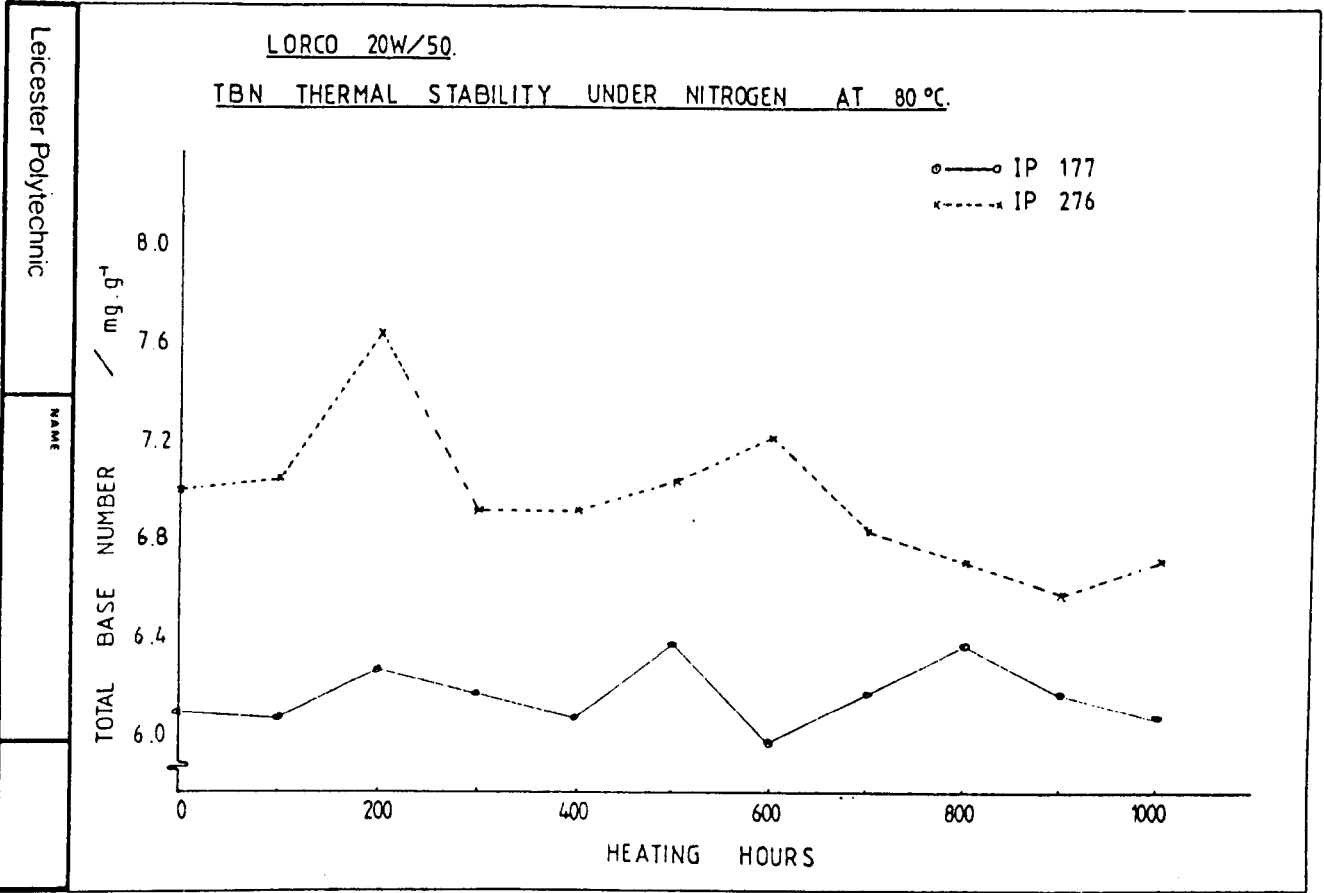


FIGURE 24.

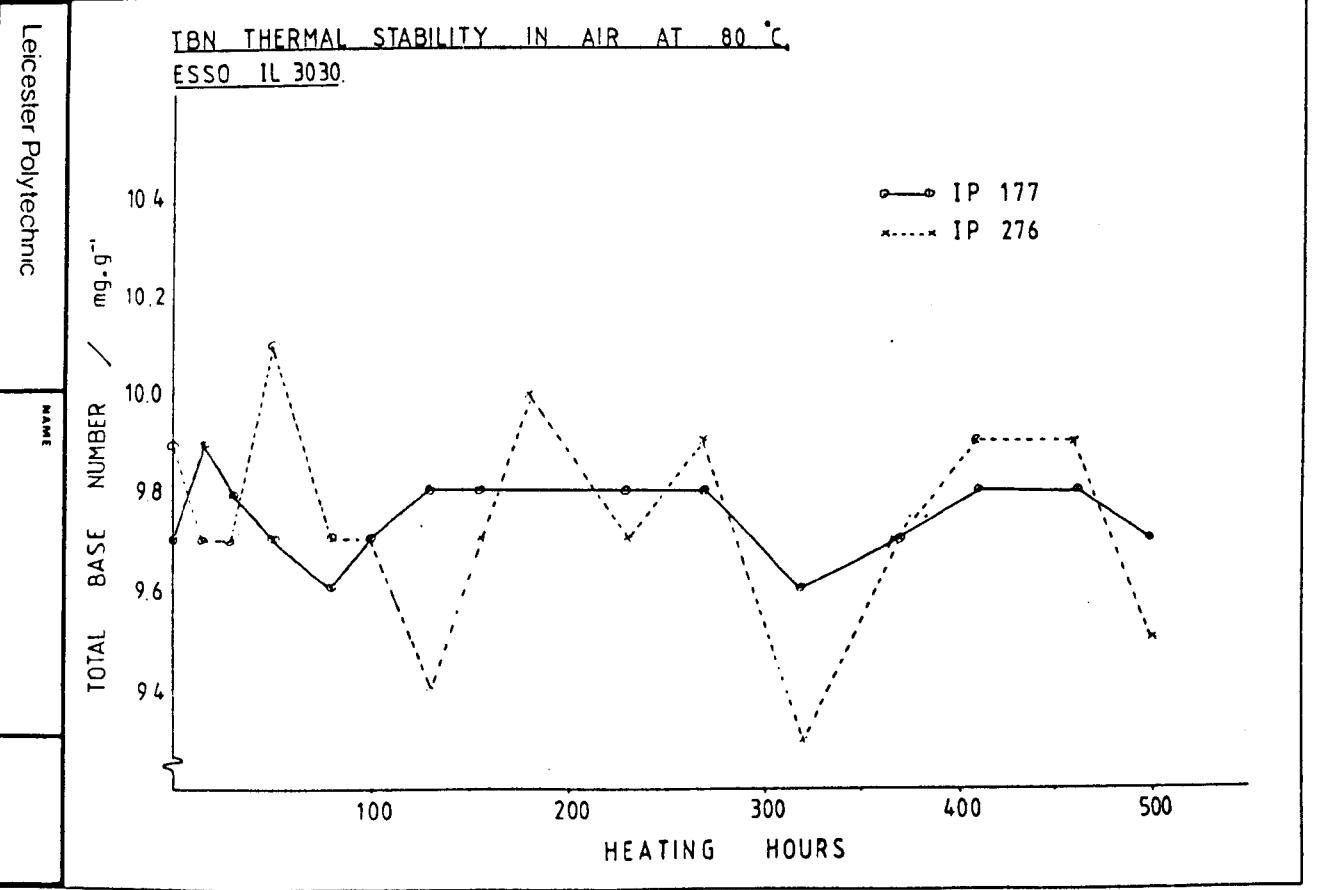


FIGURE 25.

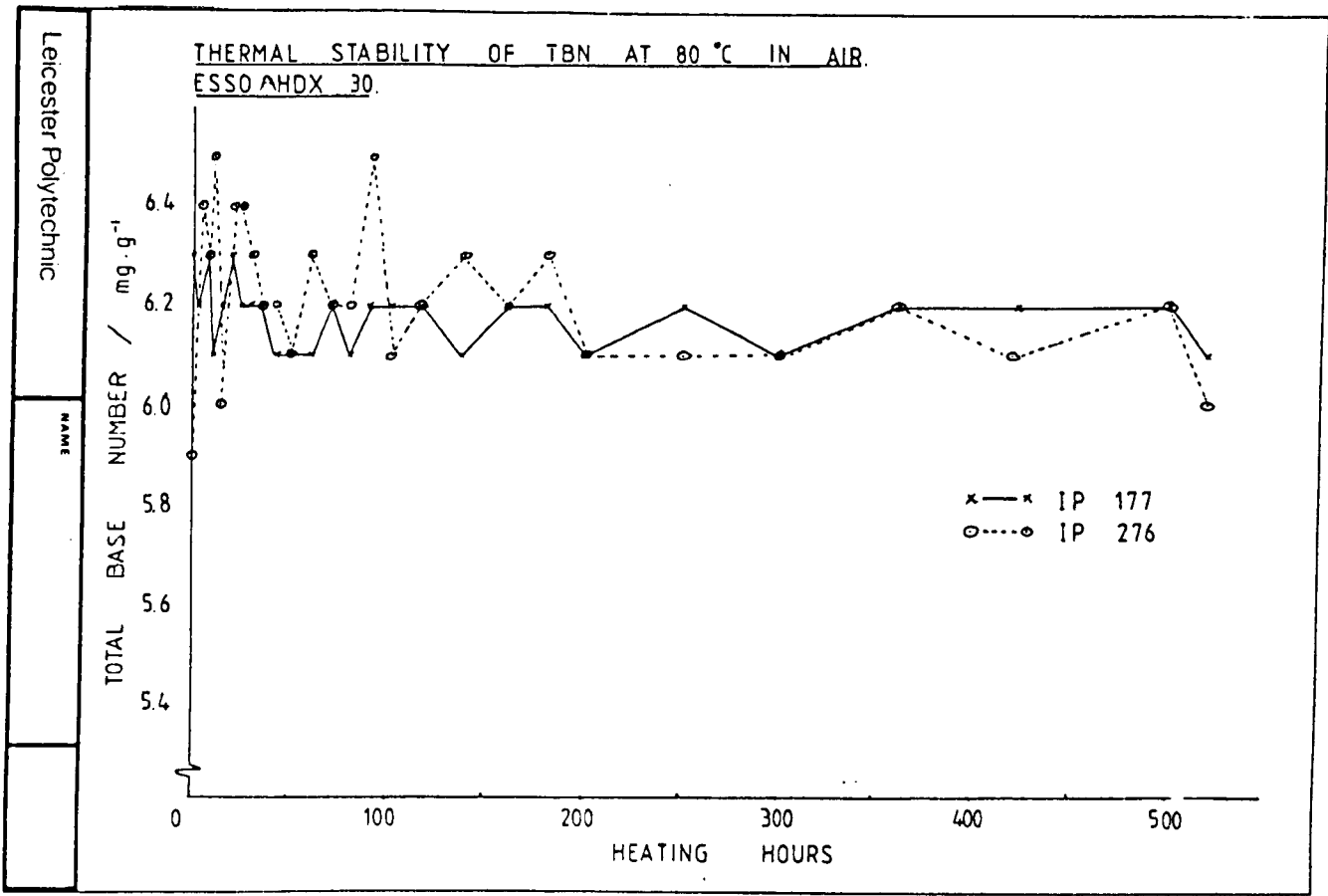


FIGURE 26.

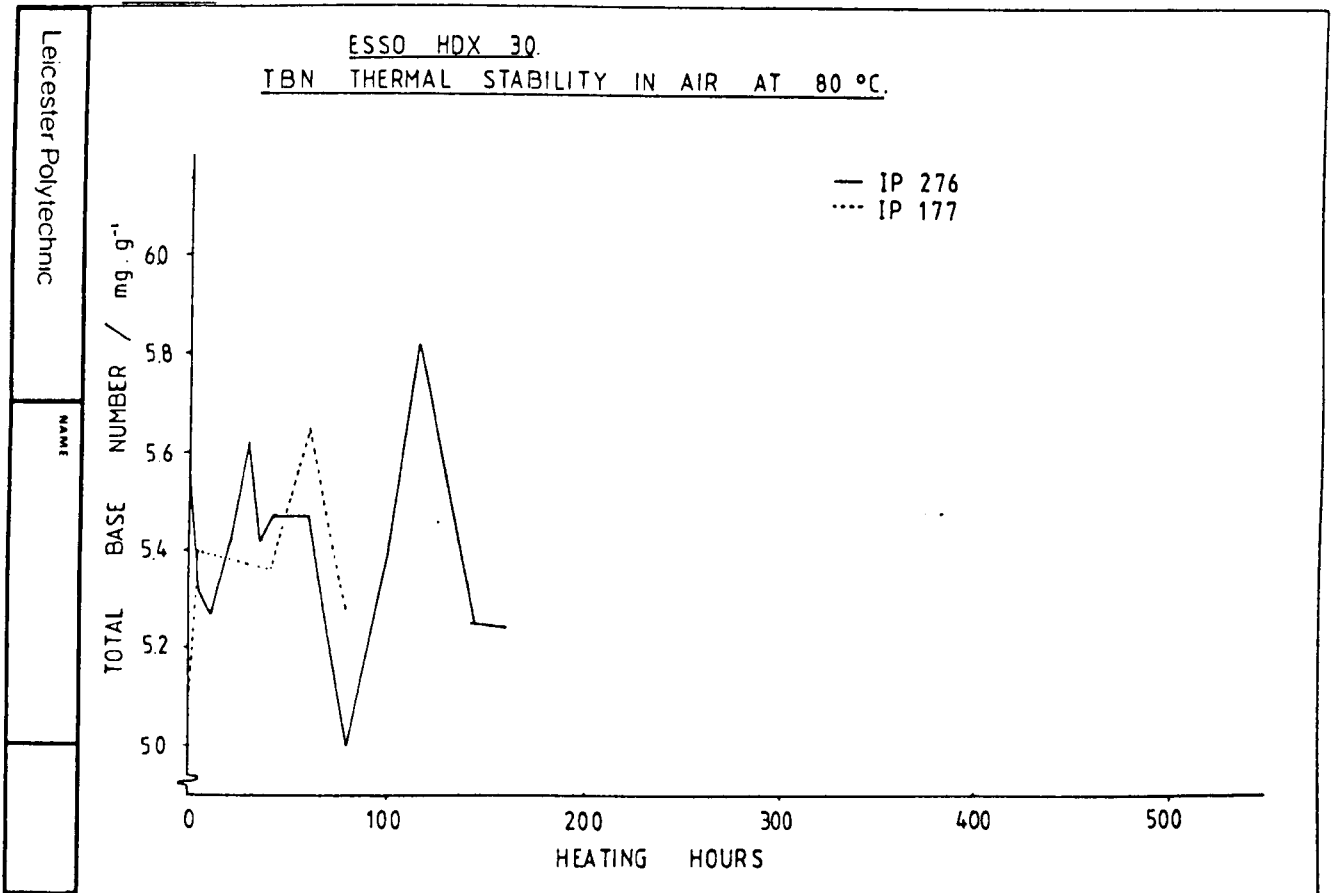
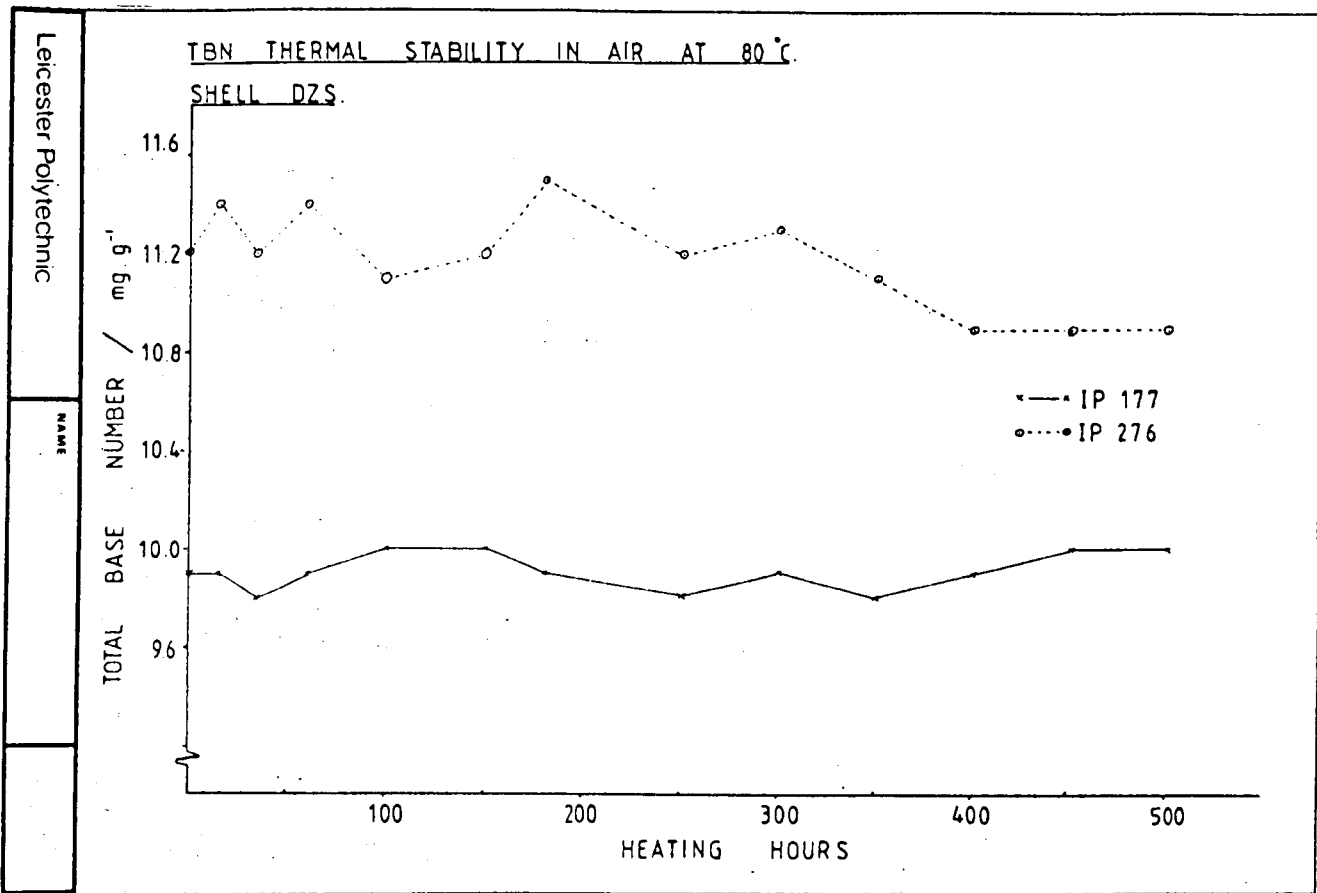


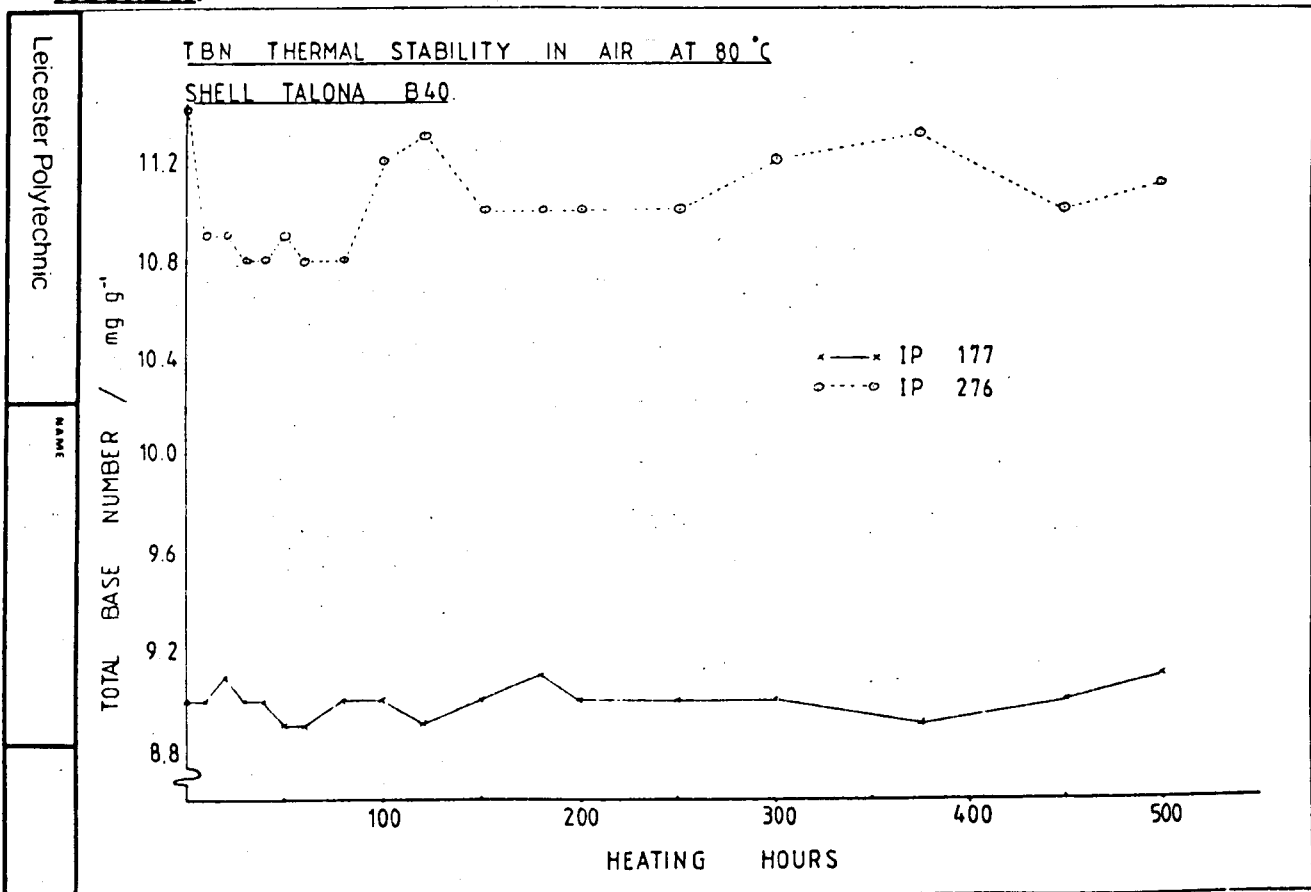


FIGURE 27.



R96

FIGURE 28.



R96

### 3.2 Total Acid Number (TAN).

The IP 177 Total Acid Number determination shares the same problems experienced in the standard IP 177 TBN determinations, arising from the common potentiometric system used, see sections 2.1 and 3.1. Lubricating oils, whether new or used, contain a wide range of 'acidic' constituents, including organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, salts of ammonia and other weak bases, acid salts of polybasic acids and detergents. The choice of potassium hydroxide as the TAN titrant in an alcoholic and essentially non-aqueous solution does not allow for effective reaction with the multitude of acid constituents during the titration. The slow reaction kinetics dictated by the solvent system is reflected by the successive maxima obtained in the titration curve, see Figure 29. To overcome the presence of such maxima, the equilibration times between titrant additions are long. The hygroscopic nature of the alcoholic potassium hydroxide solution restricts the use of very long equilibration periods.

The TAN test requires the use of buffer end-points when points of inflection cannot be obtained in the titration curve. This is usually the case for used oils which also show poor repeatability in the results obtained. These difficulties of the IP 177 TAN determination makes it impractical to automate the titration. It is for these reasons that an alternative method of TAN determination was sought. A conductimetric TAN method was investigated, based on the same IP 177 solvent system, and was found not to give a good, repeatable, end-point.

The work by Greenhow and Spencer [31] on Ionic Polymerisation as a means of End-point Indication in Non-aqueous Thermometric Titrimetry of Organic Acids was extended to oil Total Acid Number analysis. In conjunction with the Ministry of Defence, DQA/TS, Harefield, a thermometric TAN method was developed, using acrylonitrile monomer as the end-point indicator. At the end-point, when the alkali has neutralised the acid present in the oil sample, the excess alkali catalyses the polymerisation of the acrylonitrile, thus generating an exotherm. This rise in temperature is detected by a thermistor or thermocouple. A plot of temperature against titrant volume gives a clear end-point, see Figure 30.

Initial results proved successful and a search was undertaken to find a substitute for the potentially poisonous acrylonitrile. Although the use of acrylonitrile can be envisaged in a closed system, handling and cleaning (polyacrylonitrile residue) problems would still cause some concern. A short search for an acrylonitrile substitute failed to yield any positive results and, therefore, the thermometric method was refined, specifically for the Total Acid Number determination in used oils.

FIGURE 29.

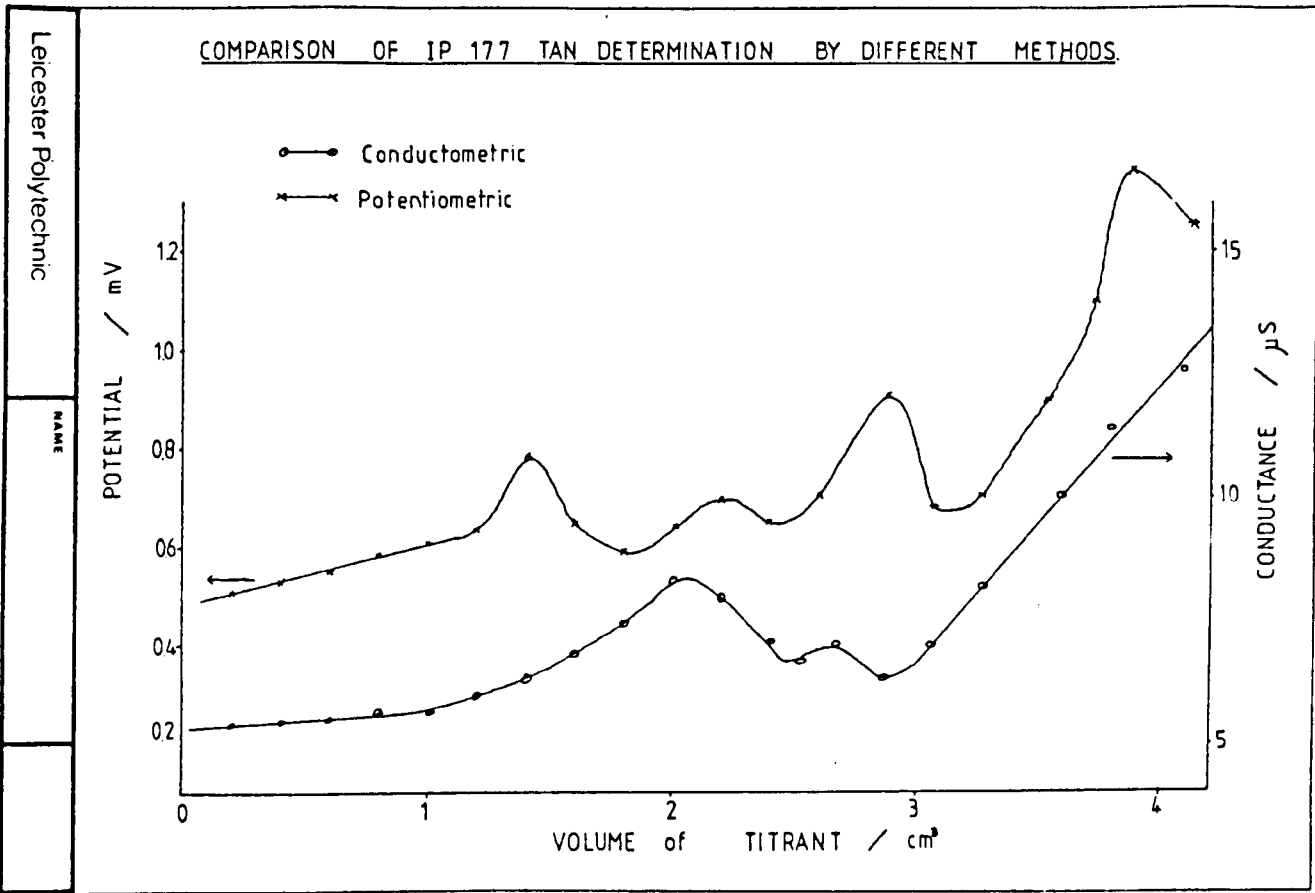
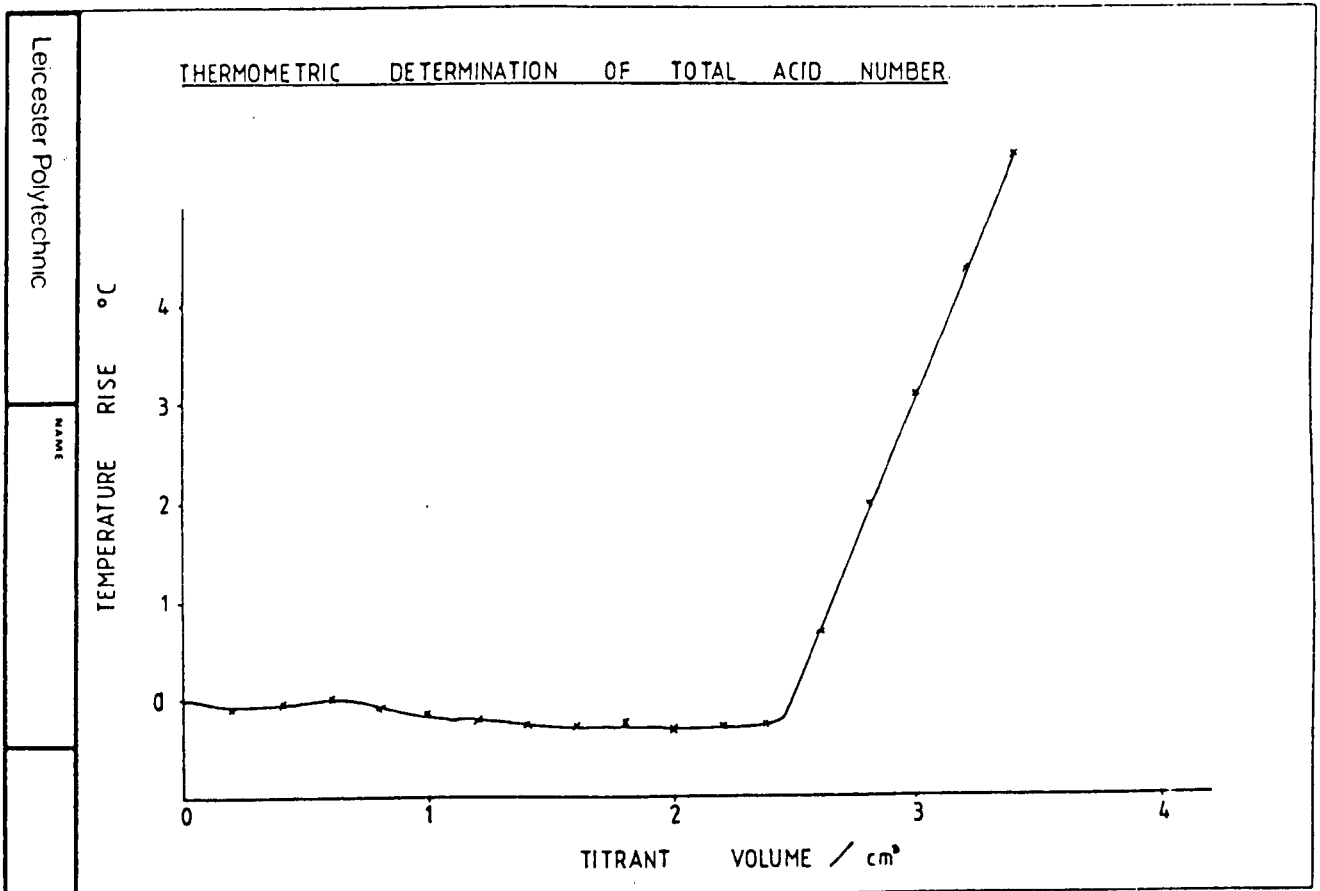


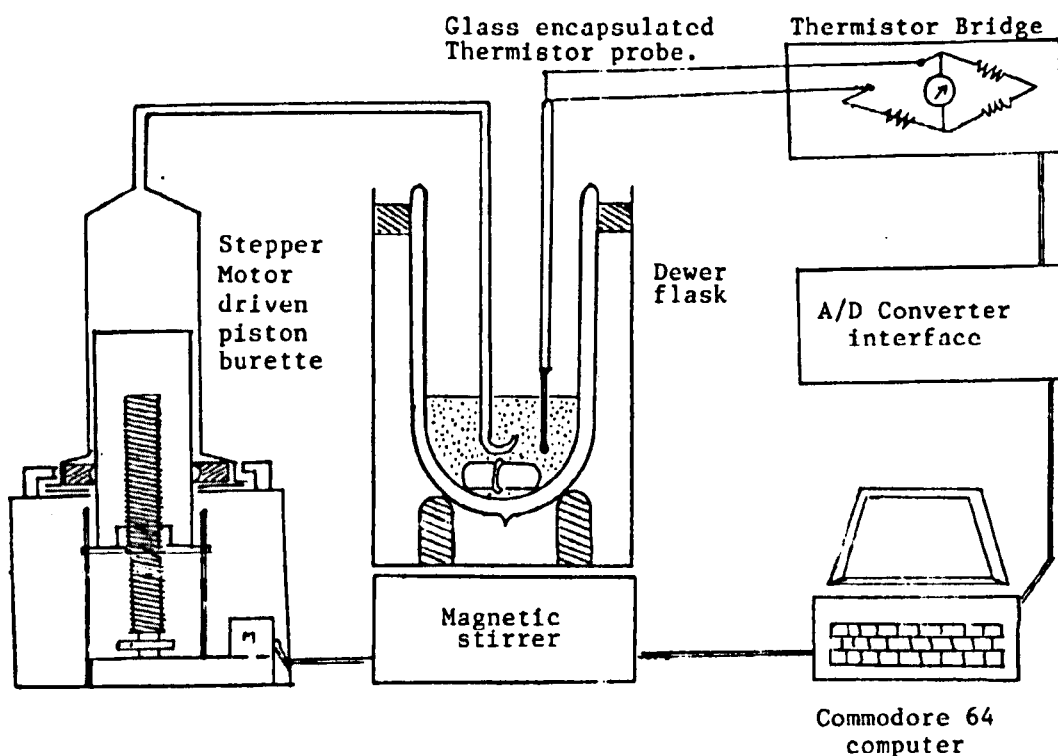
FIGURE 30.



The procedure for the thermometric determination of TAN was refined as follows;  
Figure 31:

1. A small dewar flask ( $30\text{ cm}^3$ ) enclosed in a heat insulated container was placed on a magnetic stirrer of low rotational stirring speed. A small, teflon coated magnetic follower was used to stir the reaction mixture. A sensitive glass encased bead-thermistor probe was linked to a thermistor-bridge, the output of which was recorded on a chart-recorder.
2. The titration indicator-solvent system of  $10\text{ cm}^3$  acrylonitrile,  $3\text{ cm}^3$  toluene,  $2\text{ cm}^3$  propan-2-ol and  $1\text{ cm}^3$  dimethylformamide was prepared freshly before use.
3. Oil of known mass (lg) was allowed to equilibrate for one minute in the titration solvent-indicator mixture ( $10\text{ cm}^3$ ) in the sealed dewar-flask and the thermistor.
4. The  $0.05\text{M}$  alcoholic KOH titrant was added to the mixture continuously from a computer driven piston burette, the burette-tip being immersed below the surface of the reaction mixture. Titrant was added at a rate of  $1\text{ cm}^3$  per minute. Titrant was added until a sharp rise in the thermistor output was observed on the chart recorder, which marks the titration end-point. Further addition of titrant beyond the end-point does not affect the shape of the curve. This is due to the large exotherm generated by the polymerisation of the acrylonitrile which follows the rapid chain-reaction kinetics.
5. A blank titration (one without oil sample) has to be carried out.

**FIGURE 31.** THERMOMETRIC TOTAL ACID NUMBER APPARATUS.



Studies [21, 22] show that the acids in the oils not determined by the thermometric method are weaker than  $pK_a(H_2O) = 10$  (phenol,  $pK_a$  9.89, can be determined by this method). This thermometric method works equally well for new and used oils. New oils have been found to possess high initial TAN values which may become reduced in levels with engine running before increasing due to oil degradation.

The main disadvantages of the thermometric TAN method are its toxicity (handling and waste disposal), limited shelf-life of the indicator-solvent mixture, temperature equilibration of the system-solvents-titrant, cleaning of the dewar-flask between determinations and the need to carry out a blank titration.

The advantages of the thermometric TAN method are its suitability to new, used or badly degraded oils, the rapid nature of the reaction, its relative cheapness on equipment, sample and solvents, and can be easily automated. If automated, the sealed system and small volumes will drastically reduce the occupational health hazard of using acrylonitrile.

### 3.3 DETERMINATION OF WATER IN OILS.

The IP standard methods for the determination of water were discussed in Chapter 2, section 2.9 along with its drawbacks. There are a number of physical and chemical tests that are currently used for the determination of water in non- aqueous solvents and lubricating oils. A book by Dorsey [35] gives a comprehensive treatise on the properties of water. The sections that follow give details of water determination techniques in general use and this list is by no means exhausted.

#### 3.3.1 Distillation.

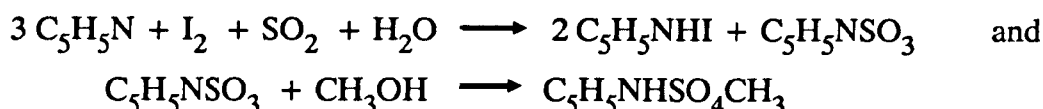
The oil can be distilled directly, or it can be mixed with a water immiscible solvent, in a Dean and Stark apparatus. On heating the oil mixture, water distils and is then condensed, collecting in the bottom of a graduated vessel where the volume of water can be ascertained. This technique for water determination is a standard Institute of Petroleum (IP 74, ASTM D95) method [22] and the procedure is given in detail in that work.

The distillation methods for the determination of water in oils requires large oil samples (1 litre or more) and prolonged heating. The presence of any volatile constituents in the oil or any ignition source may result in fires. As some of the water would be bound in the additive pack, this technique would not necessarily give a true indication of the concentration of water present in the oil. This method is too slow

and its automation, therefore, cannot even be considered for this and the above mentioned reasons.

### 3.3.2 Karl Fisher Titration.

The most widely accepted chemical method for the determination of water is the Karl-Fisher technique. A detailed description of the subject is given in the book by Mitchell and Smith [36]. The basic Karl Fisher reagent contains sulphur dioxide, iodine and pyridine in methanol. The iodine reacts quantitatively with water in the presence of methanol to form pyridine hydrogen iodide (pyridinium iodide):



The reaction is extremely sensitive to moisture and ingress of water from the atmosphere and surroundings must be prevented by the use of air tight reaction vessels. The titration process may involve both direct titration with the primary Karl Fisher reagent or back titration of the mixture. In both cases the end-point can be determined by visual, coulometric or electrometric means. A large number of Karl Fisher instruments are made commercially, having different degrees of automation and data analysis. The Karl-Fisher technique is best used for water concentrations below the 0.1% level.

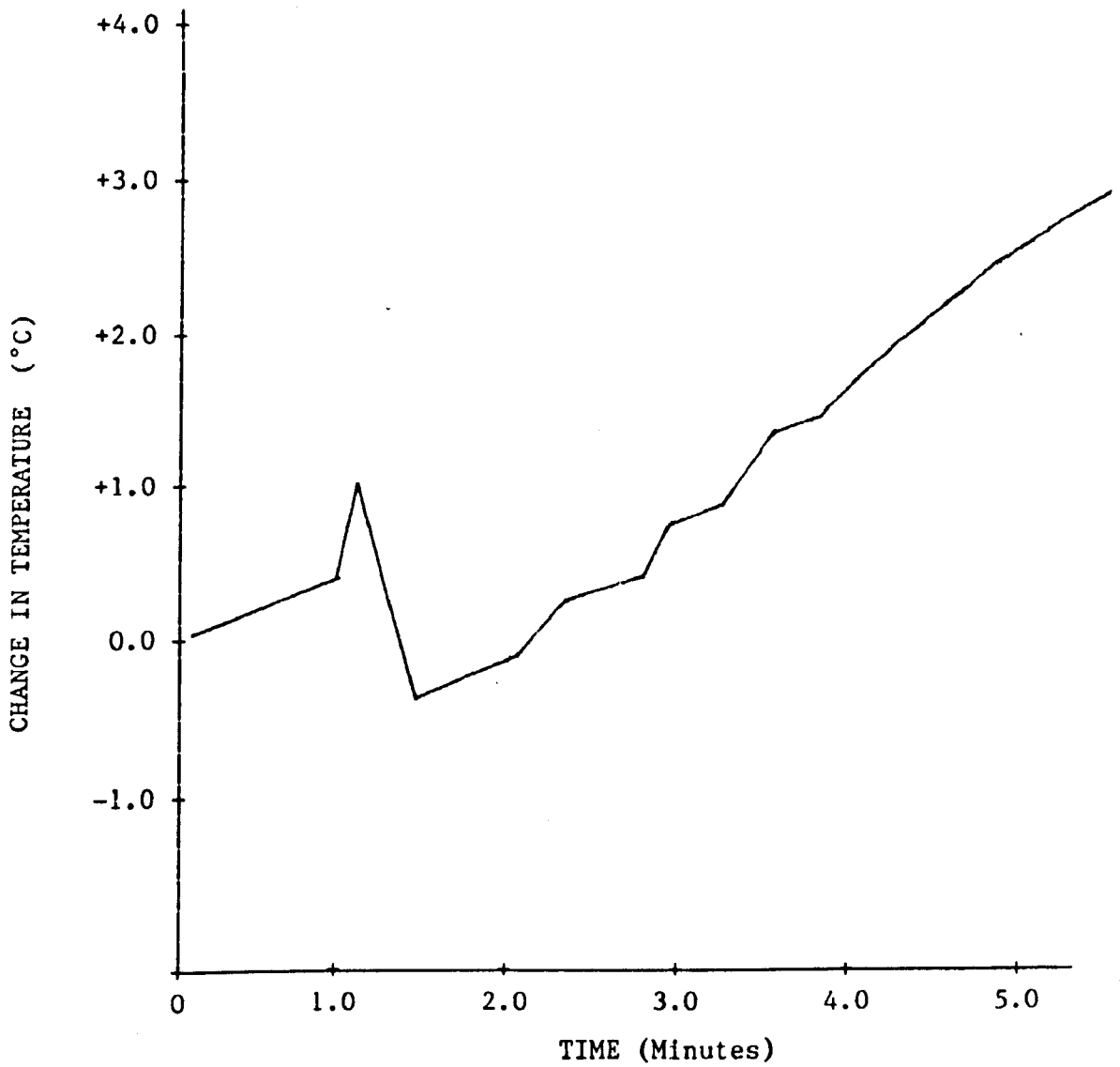
Karl-Fisher determinations of water in new oils suggest that the reagent reacts with the additive pack and with any bound water in it. In some cases it had been found that the additive (water) reaction contribution was greater than the amount of 'free' water actually present in the oil. The use of the Karl-Fisher technique must therefore be treated with caution when used with formulated lubricating oils as allowance has to be made for reaction with the additive pack, which in itself may be an unknown quantity, with used oils.

### 3.3.3 Chemical Reaction Methods.

The addition of solid and liquid chemicals to react with the water in the oil was extensively investigated. With solids such as calcium hydride, the oil appears to coat the solid reagent, preventing complete reaction and result in poor repeatability. The use of metal hydrides is not favoured for health and safety reasons due to the explosive nature of the reaction with water. Reaction of the reactants with atmospheric moisture during reactant mass determination and sample preparation was found to

be a source for inaccuracy in results. With liquid reactants, the problem of miscibility and adequate mixing must be overcome. Figure 32 shows the irregular reaction of calcium hydride crystals with water in a contaminated oil sample.

**FIGURE 32:** THERMOMETRIC REACTION CURVE OF CALCIUM HYDRIDE REACTING WITH WATER IN OIL.



### 3.3.3.1 Strong Acids.

It is well known that the addition of strong and concentrated acids to water results in the temperature of the solution to increase. The increase in temperature depends on the amount of water present, the amount of acid added and the concentration of the acid. The heat of dilution of the acid can be followed thermometrically. This method was applied to the determination of water in oils. A sensitive thermistor and thermistor bridge circuit was used to follow the titration. The solubility of concentrated sulphuric acid in oil was overcome by dissolving the oil in chlorobenzene. The amount of water was determined by comparing the temperature increase with that on a calibration chart. Despite using all possible precautions to minimise any heat losses, the repeatability of the method was found to be poor, particularly when testing used oils of known water content. It was observed that with some used oils the acid and oil mixture produced a sludge which could not easily be removed from the dewar reaction vessel. Glacial acetic acid was tried as a replacement for the concentrated sulphuric acid. The rise in temperature was as expected, lower than that obtained for the sulphuric acid (Figure 33) but, the repeatability was again poor, whether the oil was used neat or dissolved in chlorobenzene.

### 3.3.3.2 Hydrolysis of Organic Anhydrides.

The use of the hydrolysis of organic anhydrides had shown initial potential when the reaction is followed thermometrically, using a thermistor. However, the response was slow and long equilibration times were required as the reaction is kinetically a slow one. It was thought that if a suitable catalyst could be found to catalyse the hydration of acetic anhydride, then such a system would be unique to presence of water. It was, therefore, necessary to find an anhydrous catalyst that could be mixed with either the sample or the anhydride solution. The use of strong acids was precluded due to its large heat of dilution effects. The use of Friedel-Crafts catalysts in organic chemistry was investigated. Anhydrous aluminium chloride was found to be very reactive with atmospheric moisture, even when in solution. A similar salt was, therefore, sought and the search culminated in finding anhydrous stannic chloride to be a suitable catalyst.

The results of the stannic chloride catalysed hydration of acetic anhydride in water containing lubricating oils are shown in Table 25 and typical titration curves are shown in Figure 34. Although the titration appears to work well for synthetic, homogeneous, calibration mixtures of water in a special formulated synthetic oil, the reaction of the reagent with water contaminated used oils was found to be unreliable and gave different results with different lubricant formulations containing, gravimetrically, the



same amount of water. This may have been due to non-homogeneous samples as well as to differences in additive type and chemistry between the various oils tested.

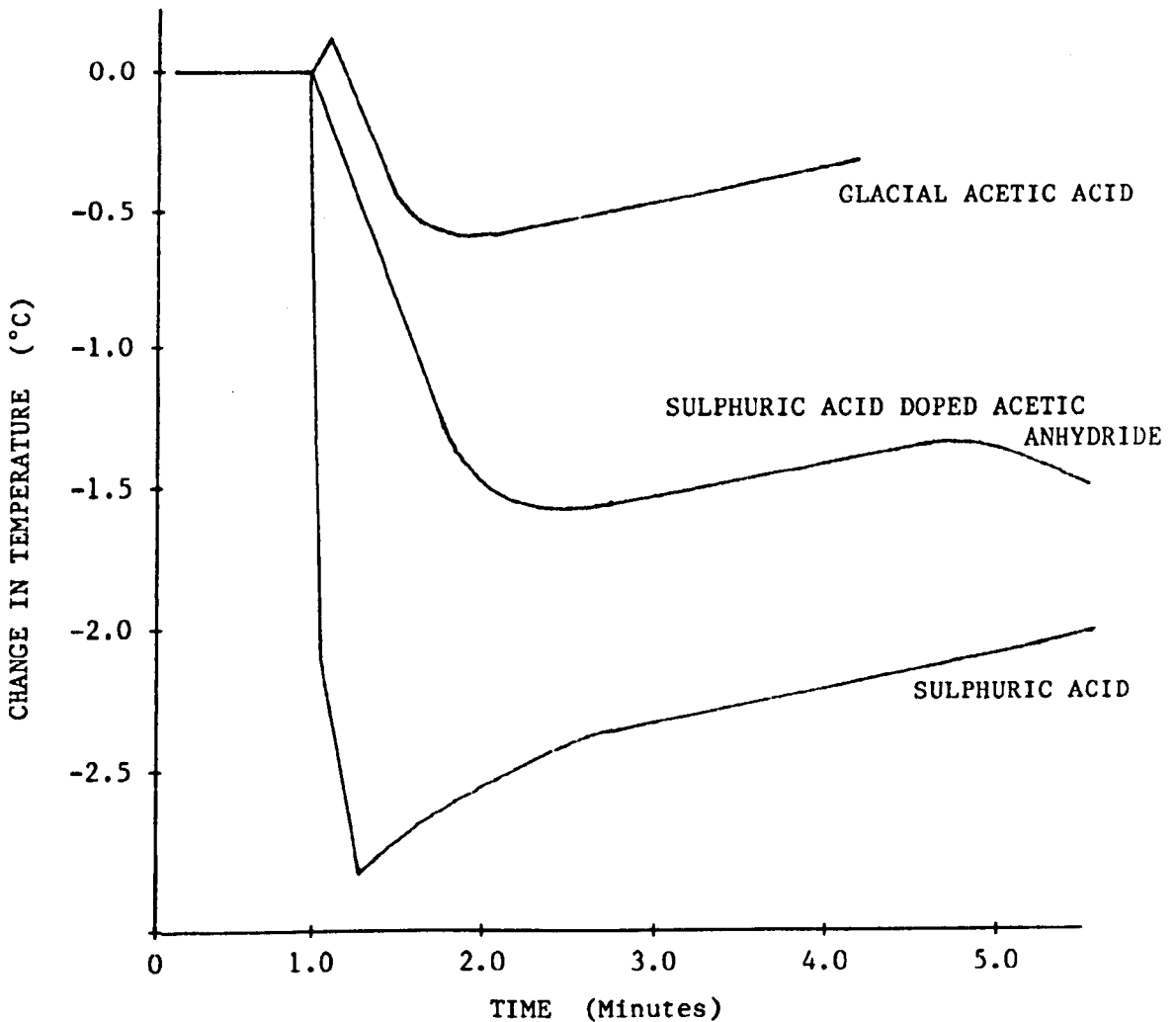
**TABLE 25:** DETERMINATION OF WATER BY STANNIC CHLORIDE CATALYSED HYDROLYSIS OF ACETIC ANHYDRIDE.

SAMPLE NUMBER	DETECTOR RESPONSE	% WATER PRESENT	% WATER BY KARL F.
0.000% STD	-5.8	0.000	0.08
0.049% STD	-4.7	0.049	0.13
0.106% STD	-4.4	0.106	0.17
0.157% STD	-3.3	0.157	0.19
0.244% STD	-3.2	0.244	0.25
0.280% STD	-2.3	0.280	0.31
0.406% STD	-0.7	0.406	0.37
0.870% STD	+4.0	0.870	0.91
New 20264	-2.0	0.320	----
2479 Used	-1.0	0.410	0.06
2650 Used	+6.0	1.050	0.60
2704 Used	-0.8	0.430	0.10
2723 Used	-0.9	0.420	0.06
2766 Used	+6.0	1.050	0.87
1146 Used	+1.7	0.660	0.20
1372 Used	-0.8	0.430	0.10
1498 Used	+0.7	0.570	0.20
1517 Used	+4.7	0.930	0.48
1610 Used	-0.7	0.440	0.26

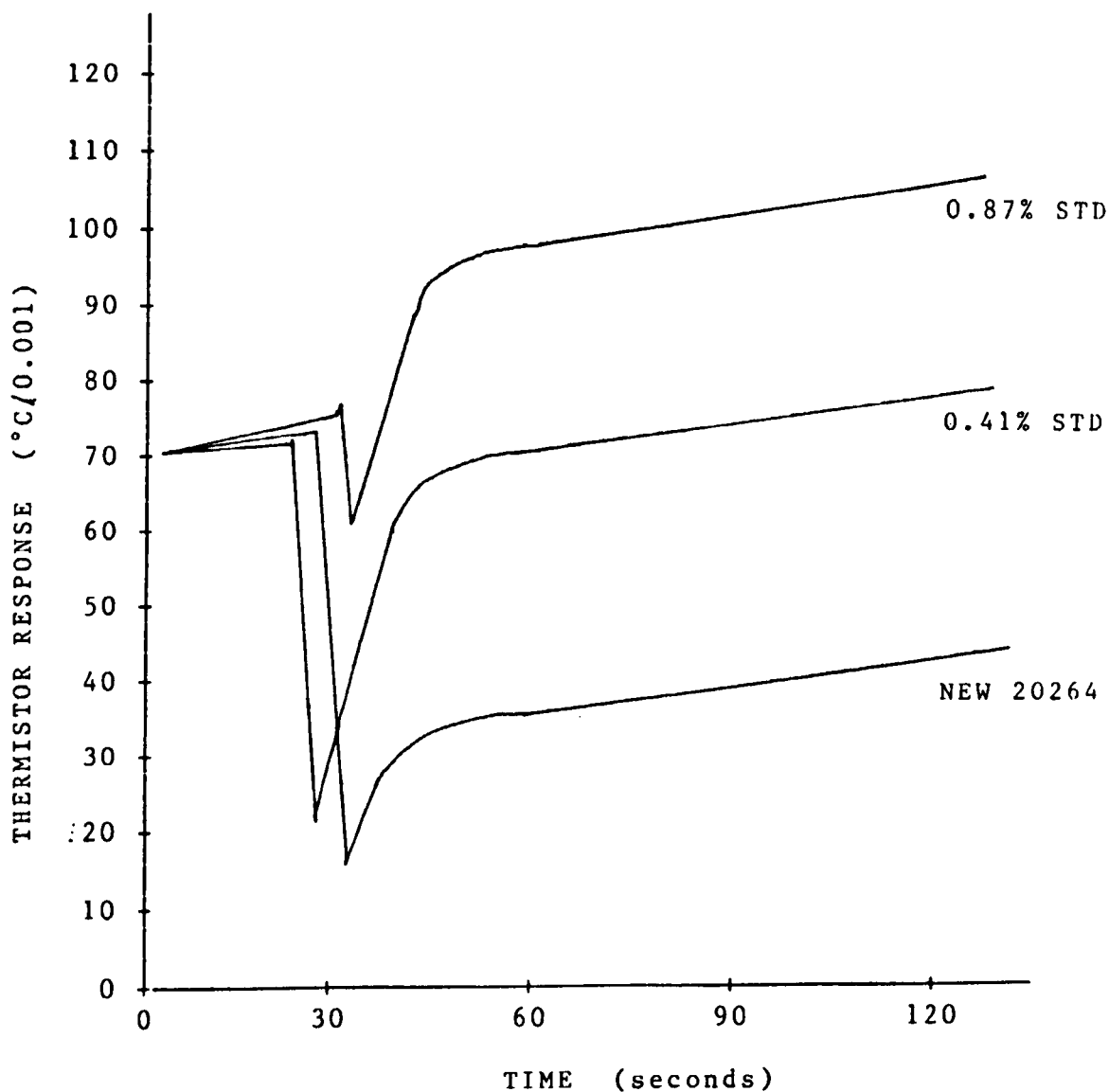
It was concluded that the stannic chloride catalysed thermometric hydrolysis of acetic anhydride was a good method for the determination of water in oils. But the method had shown variability in consistency for testing on different days and the repeatability of the method was found to vary. The reason for the lack of high levels of repeatability

and reproducibility is due to differences in ambient conditions (humidity and temperature), the integrity of the reactants and samples, and instrumental errors arising from the sensitivity and range of the thermistor bridge. However, considering these drawbacks of a thermochemical method, it was felt that a physical method for water determination would be easier to use at the railway depot level, which would be used frequently to check for water contamination in much the same way as when one checks an engines oil level. Further work on finding a better organic anhydride for use as an indicator for water content was, therefore, stopped.

**FIGURE 33** THERMOMETRIC REACTION CURVES OF 0.4% WATER IN NEW OIL (STANDARD) WITH DIFFERENT ACIDS.



**FIGURE 34** THERMOMETRIC TITRATION CURVES FOR WATER IN OILS USING STANNIC CHLORIDE CATALYSED ACETIC ANHYDRIDE REAGENT.



### 3.3.4 Chromatography.

This technique involves the injection of a small volume of oil sample into a carrier stream (gas or liquid) and this is passed through a column of porous material (stationary phase). Separation of the volatile constituents occurs and the various components appear sequentially at the detector. A peak is obtained in the output from the detector which when integrated, yields the amount of compound (water)

present in the original sample. This technique can be accurate but depends on well defined peaks and can be expensive on short column life caused by viscous used oils. The measurement time can be reduced to minutes by back flushing the column after the appearance of the water peak. This technique may find favour if the presence of other contaminants such as fuel are also to be determined.

### 3.3.5 Infrared Absorption Spectroscopy.

Infrared radiation is absorbed by water molecules at the wavelength around 1.47, 1.93 and 2.94  $\mu\text{m}$ , corresponding with the O-H bond vibration modes. The subject of infrared absorption as a quantitative analysis technique has been covered in many books and basically follows the Beer Lambert Law. Fluids of high viscosity or high opacity in the critical infrared absorption regions require the use of attenuated total reflection techniques. Used oils are generally contaminated with finely divided carbon particles which causes strong absorption/dispersion of the infrared radiation. The problem of keeping the containing cells clean and the effect of water on hydrophilic cell materials (e.g. sodium chloride cells) limits the applicability of the technique to new oils or oils with microscopic water content. Interference by overlapping or coincident infrared absorption bands by  $-\text{NH}_2$  (from amines) and  $-\text{OH}$  (from glycols and acids) groups present in used oils may result in inaccurate, high water content determinations.

### 3.3.6 Microwave Techniques.

Microwaves can be used to measure water content in three ways:

1. Absorption measurement (loss factor)
2. Dielectric measurement (dielectric constant)
3. Gravimetric techniques (selective heating)

Various instruments are available but none are satisfactory for formulated lubricating oils due in part to additives present in the oil and the problem of dissolved gases in the oil.

### 3.3.7 Other Techniques.

Moisture determination by physical techniques such as Nuclear Magnetic Resonance, Capacitance, Conductivity, or Density were found to be unsuccessful for use in determining water content in lubricating oils.

### 3.3.8 Relative Humidity - Vapour Pressure.

Henry's Law states that the mass,  $m$ , of a slightly soluble gas,  $X$ , that dissolves in a definite mass of liquid, at a given temperature, is directly proportional to the partial vapour pressure,  $p$ , of that gas.

$$m \propto p \qquad \text{Eqn. 9}$$

Water vapour approaches the behaviour of an ideal gas and, therefore, Henry's Law can be applied to liquids which contain dissolved water and exhibit well defined saturation levels. Hydrocarbons and other organic liquids have well defined saturation levels corresponding to the solubility of water in the liquid.

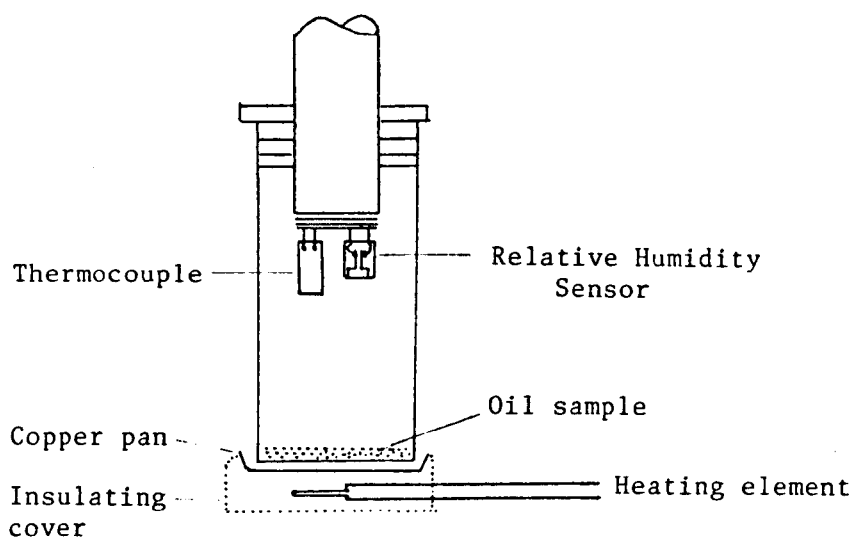
If oil is heated in a closed system, any increase in pressure, excluding that due to liquid expansion, would be due, in the main part, to volatile constituents such as fuel and water vapour. The change in pressure may be determined by the use of pressure transducers. The amount of water vapour trapped in the closed vessel can be readily determined by the use of relative humidity sensors. The latter technique was favoured for its simplicity. The main drawbacks of using the sensitive humidity detector were its ease of damage by heat and poisoning of its active surface by contaminants from the surrounding gases forming a surface film on the sensor. In addition, the technique would require that the ambient humidity of the atmosphere be kept constant, which in practice may be difficult to truly accomplish. Figure 36 shows typical results obtained for the determination of water by the relative humidity method. The cell used is shown in Figure 35.

The 'crackle test' is a technique currently used by British Rail engineers as a quick check for the presence of excessive amounts of water in engine oil. A hot, temperature controlled probe is placed into the oil and the presence of water is indicated by the crackling noise noted by the operator. This method is not quantitative but allows rapid screening of the majority of samples which do not require water analysis.

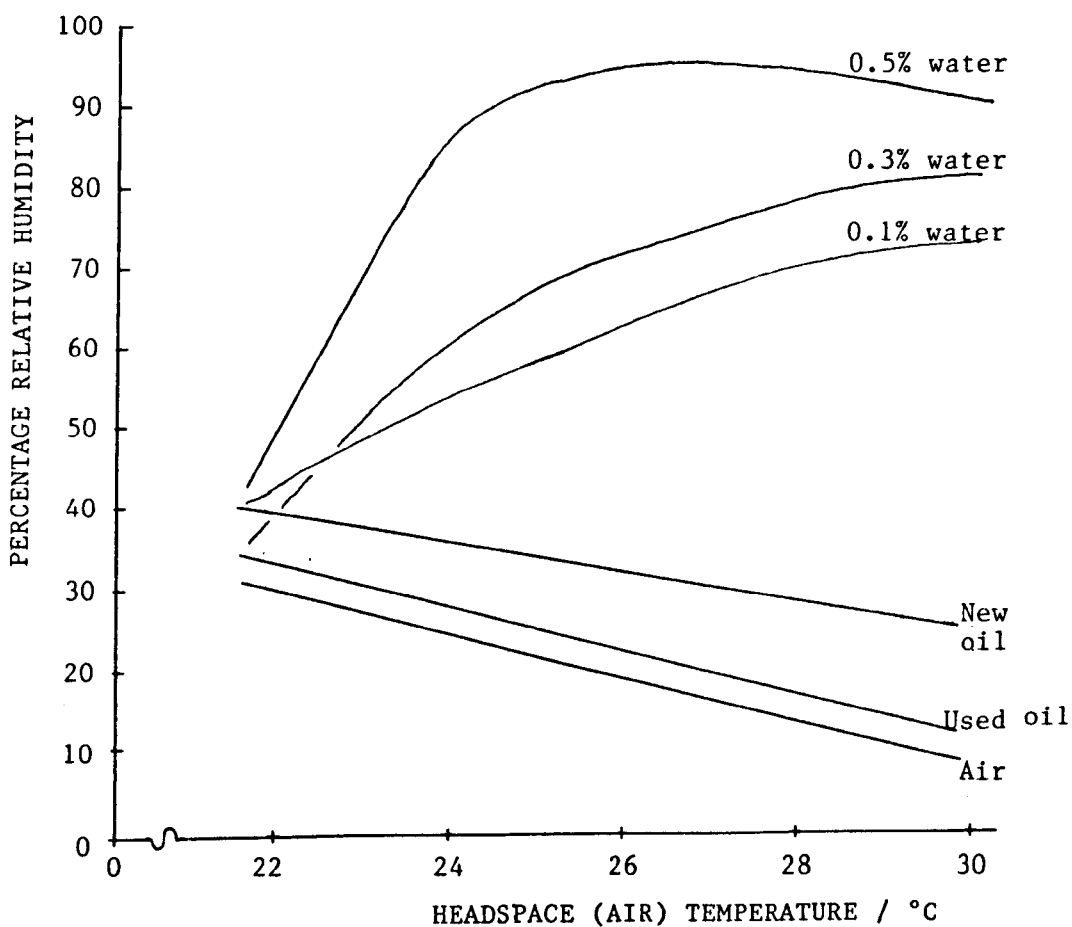
Another test employed by British Rail laboratories, for water contents in excess of 0.1%, is to completely fill a small tube with oil which is then placed in a thermostatically controlled bath (130-135 °C). On heating, steam is generated and oil is expelled. The quantity of oil left in the tube is an indication of the amount of water in the sample.

These two above mentioned tests make use of the different coefficient of thermal expansion and boiling points of water and oil, listed in Table 26, below.

**FIGURE 35.** APPARATUS FOR WATER CONTENT BY RELATIVE HUMIDITY METHOD.



**FIGURE 36.** TYPICAL RESULTS OBTAINED BY THE RELATIVE HUMIDITY METHOD.

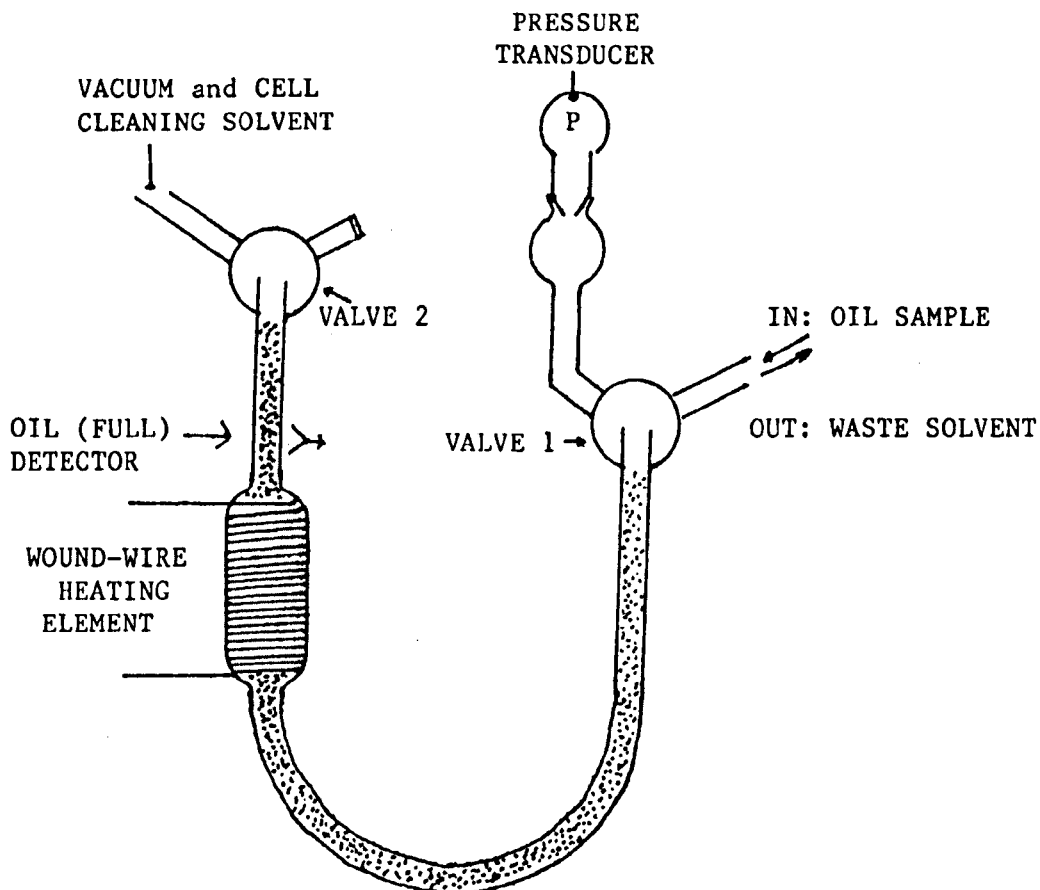


**TABLE 26. PROPERTIES OF OIL AND WATER.**

Property	Oil	Water
Boiling Point ( $^{\circ}\text{C}$ )	180-250	100
Coeff. of Expansion ( $^{\circ}\text{C}^{-1}$ )	0.0001	0.00002
Density ( $\text{g.cm}^{-3}$ )	0.84-0.90	1.00

If a given volume of oil (containing moisture) is heated in a closed vessel at a given temperature for a fixed time, then the amount of expansion would be a function of the amount of water it contains, everything else being equal. This principle was used in the apparatus shown in Figure 37. The oil was heated for a fixed time and the increase in pressure (change) was found to be proportional to the moisture content of the oil. Typical results are shown in Figure 38. This method of water determination was found to be satisfactory for use on all lubricating oil samples and could easily be automated, as shown in Figure 39.

**FIGURE 37. VOLUMETRIC THERMAL EXPANSION CELL FOR WATER IN OIL DETERMINATION BY VAPOUR PRESSURE.**



### 3.3.8.1 Calculation of water content by Relative Humidity / Vapour Pressure.

Relative Humidity is defined as the ratio of water vapour present to the pressure of vapour that would be present if vapour were saturated at the same temperature:

$$\% \text{ R.H.} = \frac{P(\text{vap})}{P(\text{sat})} \times 100 \quad \text{Eqn. 10}$$

Dalton's Law of Partial Pressures states that provided gases do not react, the pressure of a mixture of gases is equal to the sum of the partial pressures of each component making up the mixture. The partial pressure of each component is the pressure that it would exert if it alone occupied that space.

$$p = \frac{n_1 \times P}{n_1 + n_2} \quad \text{Eqn. 11}$$

where:  $p$  = partial pressure of gas 1  
 $n_1$  = number of moles of gas 1  
 $n_2$  = number of moles of gas 2  
 $P$  = Mixture (gas) pressure

The equation of state for an ideal gas relates the number of moles of a gas such that any two variables of the three variables  $P$ ,  $V$ , and  $T$  suffice to specify the state of a given amount of gas and to fix the value of the third variable.

$$P V = n R T \quad \text{Eqn. 12}$$

where:  $n$  = number of moles of gas  
 $R$  = Gas constant (8.3143 J/K/mol)  
 $T$  = Gas temperature in Kelvin  
 $V$  = Gas volume  
 $P$  = Gas pressure

Assuming that the ambient air is dry, it is possible to calculate the vapour pressure and relative humidity at a given temperature, if a water containing oil sample is heated in a closed vessel such that all the water is driven into vapour in the gas head-space. It can be assumed, under normal constant atmospheric conditions, that the air and water vapour behaviour are ideal. Consider  $X$  g oil sample of  $Y\%$  water content which is heated to  $60^\circ\text{C}$  in a dry atmosphere of a closed vessel of  $V \text{ cm}^3$  headspace, then the Relative Humidity and Vapour pressure can be calculated:

Apply Dalton's Law of partial pressures to Equation 10:



Let  $p$  = partial pressure of water vapour  
 $n_1$  = number of moles of water vapour  
 $n_2$  = number of moles of dry air  
 $P$  = total (external) pressure

Apply the Ideal gas law:

$$n_2 = \frac{PV}{RT} \quad \text{Eqn. 13}$$

Now, the number of moles of water vapour,  $n_1$ , is given by:

$$\begin{aligned} n_1 &= \frac{\text{mass in sample}(w)}{\text{Molar mass}(M)} \\ &= w/M \\ &= \frac{X \times Y}{18 \times 100} \end{aligned} \quad \text{Eqn. 14}$$

Substituting for  $n_1$  and  $n_2$  in equation (11):

$$\begin{aligned} p &= \frac{Pw/M}{w/M + PV/(RT)} \\ &= \frac{Pw}{w + PVM/(RT)} \\ &= \frac{PwRT}{wRT + PVM} \end{aligned} \quad \text{Eqn. 15}$$

Therefore, for a 0.5g oil sample containing 0.1% water which is heated to 60 °C (333 K) in a closed vessel of 10 cm<sup>3</sup> head-space, the vapour pressure generated by the water vapour is calculated as follows, given that  $R = 62.3637$ ,  $P = 760$  mmHg, and  $M = 18$  g/mol:

$$\begin{aligned} p &= \frac{w \times 760 \times 62.3637 \times 333}{w \times 62.3637 \times 333 + 760VM} \\ &= \frac{15783005 w}{20767 w + 13680 V} \\ &= \frac{760 w}{w + 0.659 V} \\ &= \frac{760 \times 0.5 \times 0.1/100}{0.5 \times 0.1/100 + 13680 \times 10/1000} \\ &= 53.62 \text{ mmHg} \end{aligned}$$

The partial vapour pressure at a given temperature and pressure, depends upon the mass of water vaporised and its containing volume. The relative humidity of the head-space above the heated oil sample depends on the (initial) ambient relative humidity and the final temperature and pressure of the head-space. The change in relative humidity will be greatest if the initial relative humidity of the air is zero (dry air); for example, for the above sample (saturation water vapour pressure at 60 °C = 149.41 mmHg):

$$\begin{aligned} \text{RH}\% &= \frac{P(\text{vap})}{P(\text{sat})} \times 100 \\ &= \frac{52.62 \times 100}{149.41} \\ &= 36\% \end{aligned}$$

If the ambient relative humidity is 70% then the final relative humidity would be 78%. Therefore, the relative humidity increase can only be used to indicate the qualitative presence of water under unknown or varying ambient relative humidity conditions. It has been shown above that quantitative levels of water can be determined by the relative humidity method, provided that the following conditions can be fulfilled:

1. The initial humidity in the apparatus is maintained at a known (low) relative humidity, before heating of the oil commences.
2. Leaks into or out of the apparatus are eliminated.
3. No water from the sample is allowed to escape during any purging/drying to achieve condition (1) above.
4. Equilibration times for achieving a stable (low) relative humidity should be neither too short nor too long as conditions (1) and (3) may be compromised.
5. All the water in the oil must enter the head-space as water vapour.

The maximum change in relative humidity that is possible to determine water contents between 0.05% and 0.25%, in dry air, is (RH) 18.6% and (RH) 81%, respectively. Therefore, in order to avoid saturation of the head- space, the maximum initial ambient relative humidity should not exceed 20%.

### 3.3.8.2 Relative Humidity Experimental Method.

A miniature solid-state relative humidity sensor and amplifier was obtained and used to determine the water content of lubricating oils in a closed vessel. The relative humidity cell consisted of a pair of thin, precious metal plate electrodes etched onto

a special glass-polymer surface, the surface of the electrodes being coated with a humidity sensitive polymer. The working temperature range of the humidity sensor being between 5 and 80 °C. The sensitive surface of the sensor was susceptible to contamination by oil films, halogenated solvents and water. These contaminants and excessive heat could irreversibly damage the operation of the sensor. For this reason, the sensor was located as far away as possible from the heat source and the oil sample. The apparatus consisted of the humidity sensor, a thermocouple, and a small heating source, all of which were interfaced and controlled by a computer. The computer controlled the heater, either for a set heating period or until a set temperature was reached, during which the relative humidity data was measured and read by the computer. The method involved placing a known mass of oil (1-5 g) in a clean, dry, (30 cm<sup>3</sup>) glass-bottle and sealing it with an air-tight stopper through which the thermocouple and relative humidity sensor were installed. The bottle and its contents were allowed to stand up-right on a small heating element (plate) that had a diameter comparable to that of the base of the glass container (see Figure 35).

Typical results of various oil samples heated by this method are shown in Figure 36. The results obtained show that the method can be used both qualitatively and quantitatively, see Table 27. New oils and oils containing no water show a decrease in relative humidity as the oil is heated. Oils containing water show an increase in relative humidity in proportion to the water content.

These initial results showed the viability of the method but the main draw-backs explained above, especially that of chemical contamination (short life) of the sensor and its high replacement cost, make this a technique not suitable for routine testing, particularly at the depot level for which it was intended.

### 3.3.9 Water Determination by the Vapour Pressure Method.

The relative humidity method for the determination of water revealed that the volatility of water could be exploited to determine its level in the non-volatile oil. This may be simply achieved by heating the oil to 100 °C or more in a closed container and measuring the change in the pressure of the air head-space above the oil. If a constant volume of oil is used each time in the same heating vessel, then any change in pressure would be due to volatile components present in the oil and Daltons law of partial pressures can be applied assuming that the gases behave as perfect gases over the temperature range. The change in pressure due to the temperature increase of the system and its contents and that due to the expansion of the oil would be constant and can, therefore, be ignored.

**TABLE 27. DETERMINATION OF WATER BY RELATIVE HUMIDITY.**

SAMPLE NUMBER	DETECTOR RESPONSE	% WATER PRESENT	% WATER BY KARL F.
0.000% STD	1.0	0.000	0.08
0.049% STD	5.0	0.049	0.13
0.106% STD	8.0	0.105	0.17
0.157% STD	11.0	0.157	0.19
0.244% STD	14.0	0.244	0.25
0.280% STD	-2.3	0.280	0.31
0.406% STD	18.0	0.406	0.37
0.870% STD	26.0	0.870	0.91
NEW 20264	-14.0	0.000	-.---
1146	48.0	> 2.000	0.20
1372	2.0	0.015	0.10
1498	5.0	0.050	0.20
1517	48.0	> 2.000	0.48
1610	3.0	0.030	0.26
1617	-8.0	0.000	0.23
1677	32.0	1.400	0.10
1685	11.0	0.150	0.60
1933	-11.0	0.000	0.16
2479	29.0	1.100	0.06
2650	45.0	> 2.000	0.60
2704	5.0	0.050	0.10
2723	-1.0	0.000	0.06
2746	40.0	> 2.000	0.87

The requirements for a method for determining water content based on pressure rise due to volatility is as follows:

1. A sealed container containing a known or fixed quantity of oil sample (1 - 5g), a pressure sensor and an external heating source.
2. The system must be at a stable, low temperature initially, without resulting in any loss of volatile components.
3. Safety features to prevent accidents due to excessive rise in temperature or pressure must be incorporated.
4. The heat transfer to the oil sample must be rapid and uniform for a duration of either a fixed time or until a set temperature is reached.
5. The quantity of oil volume and air head-space must be sufficient to comply with requirements (3) and (4) above, and to have an optimised working range covering the expected water content (0.05% to 0.25%).

6. The pressure sensor must have a wide temperature and pressure working range and must be sufficiently accurate and robust to measure small and rapid changes in pressure.
7. The system must lend itself to automation with a cycle time of less than four (4) minutes between successive determinations.

**TABLE 28. DETERMINATION OF WATER BY VAPOUR PRESSURE.**

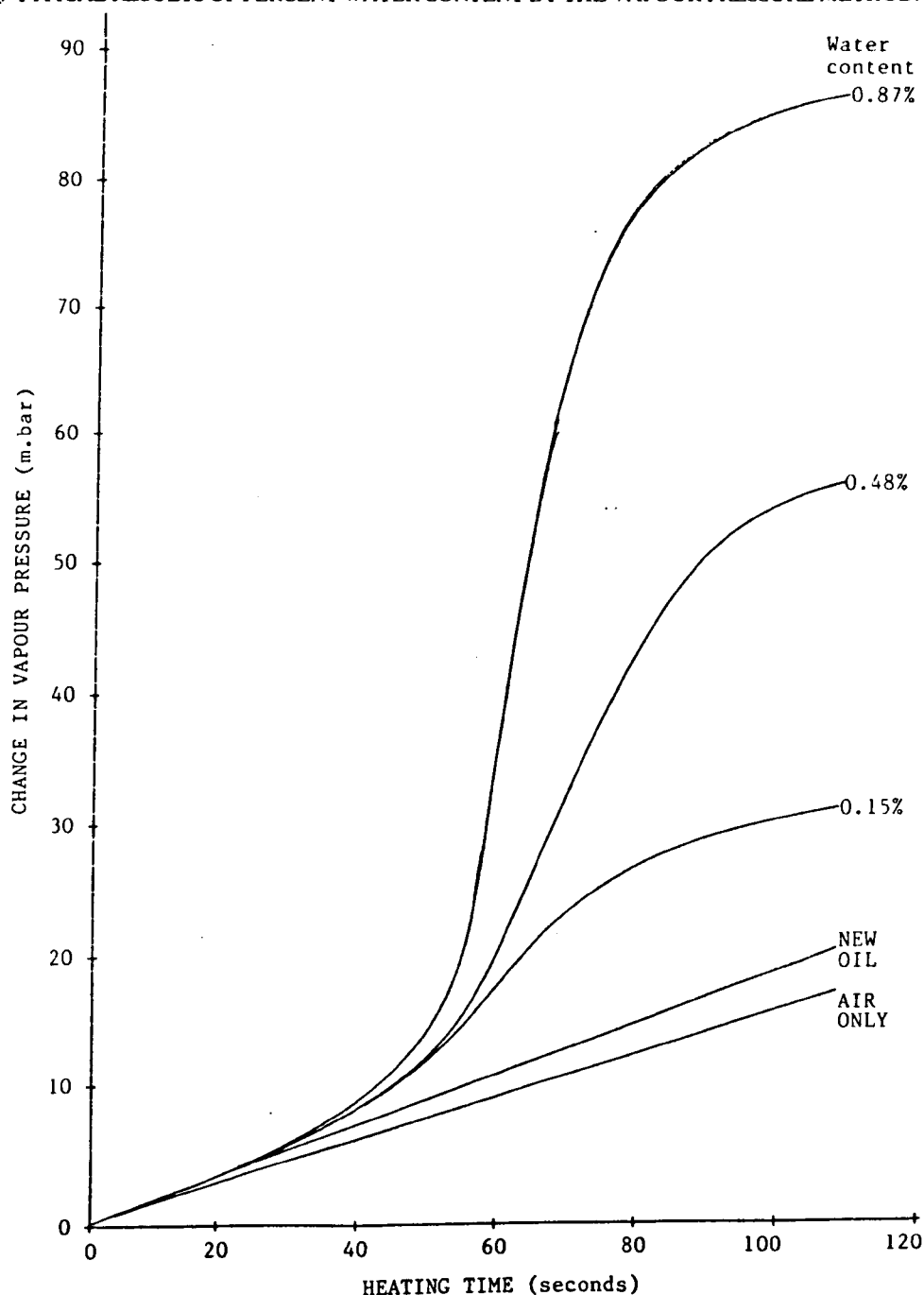
SAMPLE NUMBER	DETECTOR RESPONSE	% WATER PRESENT	% WATER BY KARL F
0.000% STD	-5.8	0.000	0.08
0.049% STD	-4.7	0.049	0.13
0.106% STD	-4.4	0.105	0.17
0.157% STD	-3.3	0.157	0.19
0.244% STD	-3.2	0.244	0.25
0.280% STD	-2.3	0.280	0.31
0.406% STD	-0.7	0.406	0.37
0.870% STD	4.0	0.870	0.91
NEW 20264	--2.0	0.302	-.---
1146	1.7	0.651	0.20
1372	-0.8	0.415	0.10
1498	0.7	0.557	0.20
1517	4.7	0.934	0.48
1610	-0.7	0.406	0.26
1617	0.1	0.500	0.23
1677	0.3	0.519	0.10
1685	0.6	0.547	0.60
1933	-1.4	0.358	0.16
2479	-1.0	0.396	0.06
2650	6.0	1.057	0.60
2704	-0.8	0.415	0.10
2723	-0.9	0.406	0.06
2746	6.0	1.057	0.87

A system was developed to meet the above requirements. Work began by checking the viability of the method. Oil (5g) was drawn into a small bore (5mm) glass U-tube which was sealed at one end by a valve and at the other end, a pressure transducer was placed as far away from the oil as possible to avoid problems. The pressure transducer was connected to a Commodore 64 micro-computer which read the pressure data. A heating wire element was wound round a section of the tube containing the oil. Power

was supplied to the heating element, the duration of which was controlled by the computer. The initial and final height of the oil level in the tube-end containing the pressure transducer, was noted visually. Figure 39 shows the layout of the system. The results of oil samples containing different levels of water are shown in Tables 28 and 29, and Figure 38.

The technique developed for the determination of water by this method is easily automatable and has been incorporated into the single computer controlled unit which also analyses the Total Base Number and the Percentage Total Insoluble Matter.

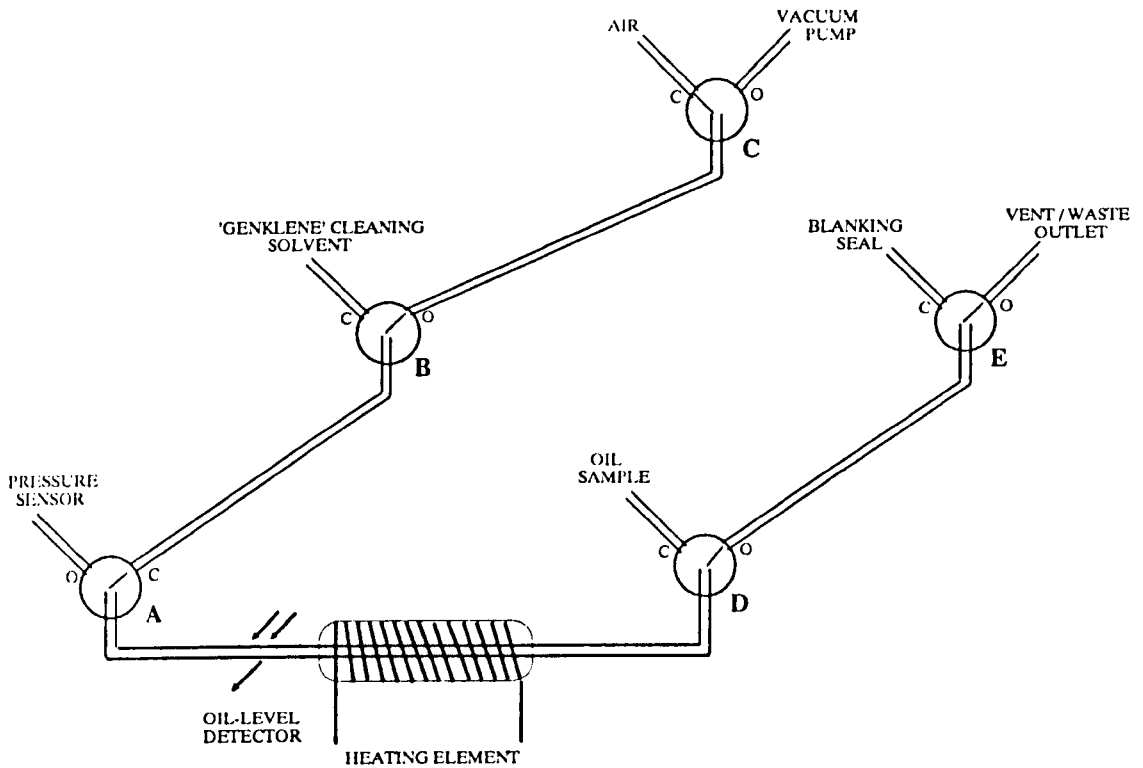
**FIGURE 38.** TYPICAL RESULTS OF PERCENT WATER CONTENT BY THE VAPOUR PRESSURE METHOD.



### 3.3.10 Conclusions.

The determination of water based on the generation of vapour pressure by heating the oil sample to 100 °C (or above), in a closed vessel has been shown to be a viable technique and covers the water content range of 0.05% to 0.5%. The method is simple, accurate and repeatable. The results obtained by this method is comparable with those obtained by other methods and is in agreement with the relative humidity method. This technique can be considered to be superior to some of the techniques discussed previously in that its results can be shown to be correct both gravimetrically and theoretically as shown in the derivations and calculations above, assuming that there is no chemical trapping or reaction of any water present in the oil.

**FIGURE 39.** WATER BY VAPOUR PRESSURE SYSTEM CONFIGURATION.



**TABLE 29.** RESULTS OF WATER CONTENT DETERMINATION BY VAPOUR PRESSURE METHOD.

SAMPLE	Vapour pressure% increase (mbar).	WATER CONTENT
New oil	18	0.00
0.05% STD	20	0.05
0.10% STD	25	0.10
0.15% STD	29	0.15
0.20% STD	34	0.20
0.25% STD	39	0.25

### **3.4 DETERMINATION OF TOTAL INSOLUBLE MATTER IN OILS.**

The combustion of any hydrocarbon in the presence of oxygen results in the formation of water, carbon dioxide and partially oxidised compounds such as aldehydes and nitrogen oxides. In the case of combustion where the amount of hydrocarbon is considerably in excess to the amount of oxygen available to completely oxidise the hydrocarbon, soot formation occurs. These products of incomplete combustion enter the lubricating oil through blowby and accelerate the oxidative degradation of the oil.

It can be argued that the presence of finely divided wear debris further assists in the degradation of the oil and results in the abrasive wear of the engine. The lubricating oil in internal combustion engines can be observed to become discoloured with engine operational time. The presence of soot, wear debris and partially oxidised material in the oil eventually changes the oil's physical and chemical characteristics such that it may damage the mechanical integrity of the engine. This would arise due to resinous material of high molecular mass being formed which may become deposited in oilways and various other parts of the engine thereby causing inadequate lubrication and heat transfer. The presence of resins of high molecular mass may also increase the viscosity thus; further impairing the operation of the engine, especially during starting. It is therefore important that the lubricating oil is changed regularly, or better still, as soon as it is likely to be a cause of concern.

#### **3.4.1 Comparison of TIM Methods of Determination.**

The state of the oil can be easily ascertained by noting its viscosity, colour and smell. These subjective tests may be difficult for the untrained person and is probably a carcinogenic health risk if it is done frequently. Therefore, an easy physical test is needed. Many types of oil viscosity checks are in use, including a simple timed-flow comparator between a new and a used oil. The quality of "smell" between oils of varying stages of degradation is subjective and is unlikely to be used, except by those who have a professional "nose" for it and its practice cannot be recommended for health reasons. The amount of 'dirt' present in the used oil is quantified as the percentage of Total Insoluble Matter (% TIM) it contains. There are a number of standard physical measurements currently in use to determine % TIM, ranging from optical methods to thermogravimetric analysis. The blackness of an oil can be determined by various instrumental techniques based on light radiation and absorption characteristics of the oil. Alternative tests such as the blotter spot test, the solids in engine oil test (IP 316), the "pentane insolubles" and "toluene insolubles" (IPD892) tests, the ash content (IP4), and the carbon residue tests (IP 13, IP 14) are used but suffer from drawbacks.



In the case of the oil-blotter spot test, the main drawbacks are its range (3% TIM maximum), repeatability, time taken to develop a reasonably sized spot and its interpretation with the view to automation. The solids in engine oil (IP 316) test and the “pentane insoluble” test requires the use of *n*-heptane and *n*-pentane oil mixtures, respectively, to be centrifuged at high speeds with some risk of danger, poor repeatability of the test arising from dilution errors and the problems of interpretation and the difficulty of automation. In addition, it is known that oils containing large proportions of detergent or dispersant additives give erroneous results due to deposition of additives or to incomplete sedimentation.

### 3.4.2 Determination of TIM by Light Absorption Method.

Figure 40 shows typical infrared absorption spectra for new and used oils, diluted in hexane. The spectra show good absorption windows between 1800 - 2000 (cm<sup>-1</sup>) and 3700 - 3900 (cm<sup>-1</sup>) wavenumbers for used oils (1% m/v in hexane). The 1800-2000 (cm<sup>-1</sup>) wavenumber window has no interference from any other vibrations in that region and is therefore suitable for measuring oil blackness levels. However, British Rail preferred a white light source which meant that the infrared based measurements would be a second choice for % TIM determinations. Figure 41 shows typical ultra-violet/visible (uv/vis) spectra of 1% m/v oil samples in the IP 276, glacial acetic/chlorobenzene (1:2 v/v), solvent mixture. The uv/vis spectrum of the diluted oil samples show absorption bands below 350 nm but no significant absorbances above 400 nm. The uv/vis spectrum in the region 400 nm to 850 nm coincides with the white light preference by British Rail and was therefore adopted for % TIM measurement.

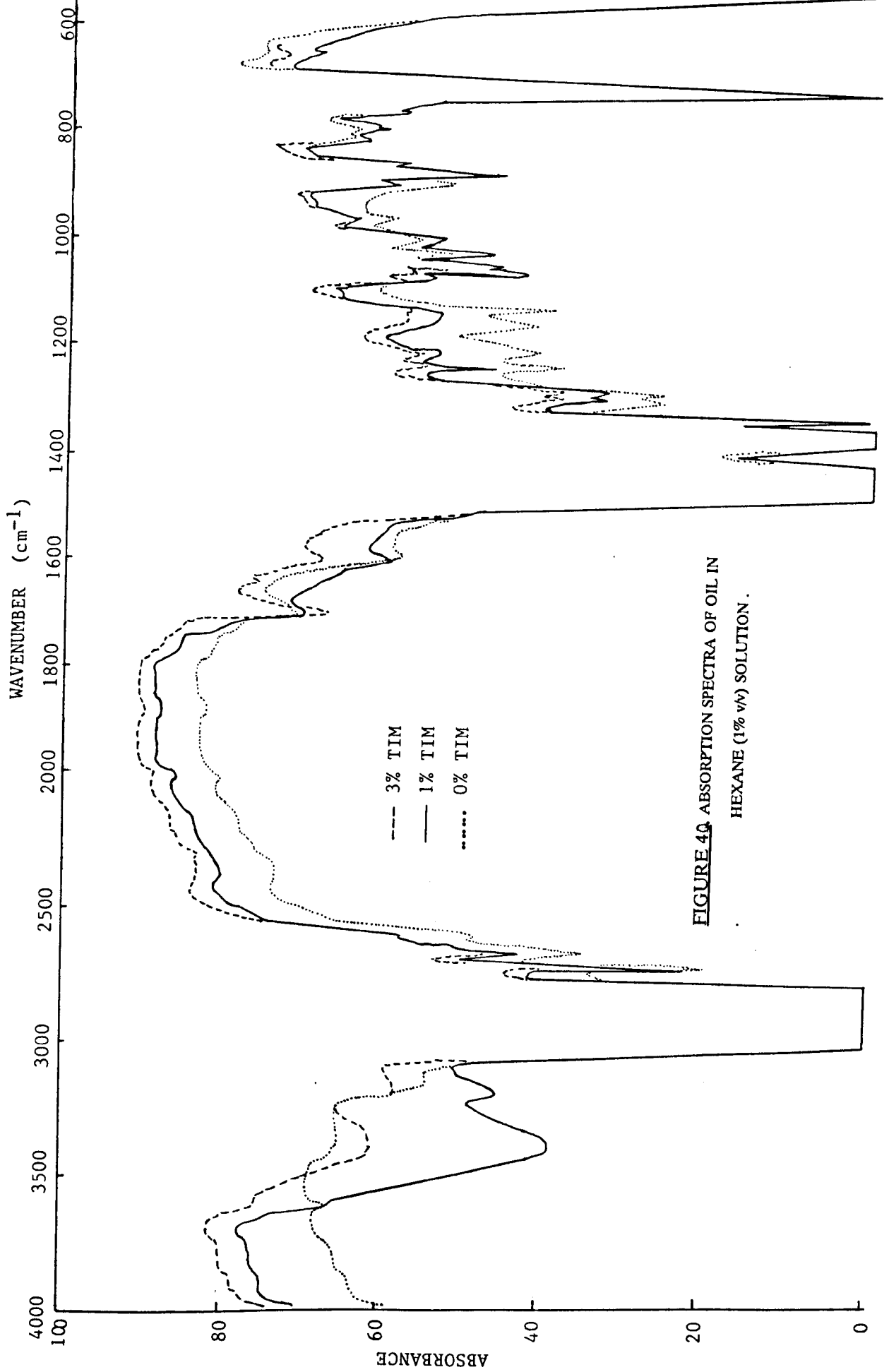
The determination of Total Insoluble Matter (TIM) by optical methods relies on the Beer-Lambert Law. The Beer-Lambert Law is a combination of Beer’s Law and Lambert’s Law:

#### 3.4.2.1 Lambert’s Law.

This law predicts the effect of the thickness of a sample medium upon the fraction of incident radiation which is absorbed. Lambert reached the conclusion that each unit length of material through which radiation passes, absorbs the same fraction of radiation. For a given monochromatic beam of incident radiation of intensity  $I_0$ , passing through a thickness ( $b$ ) of absorbing material, the reduction in intensity can be stated as:

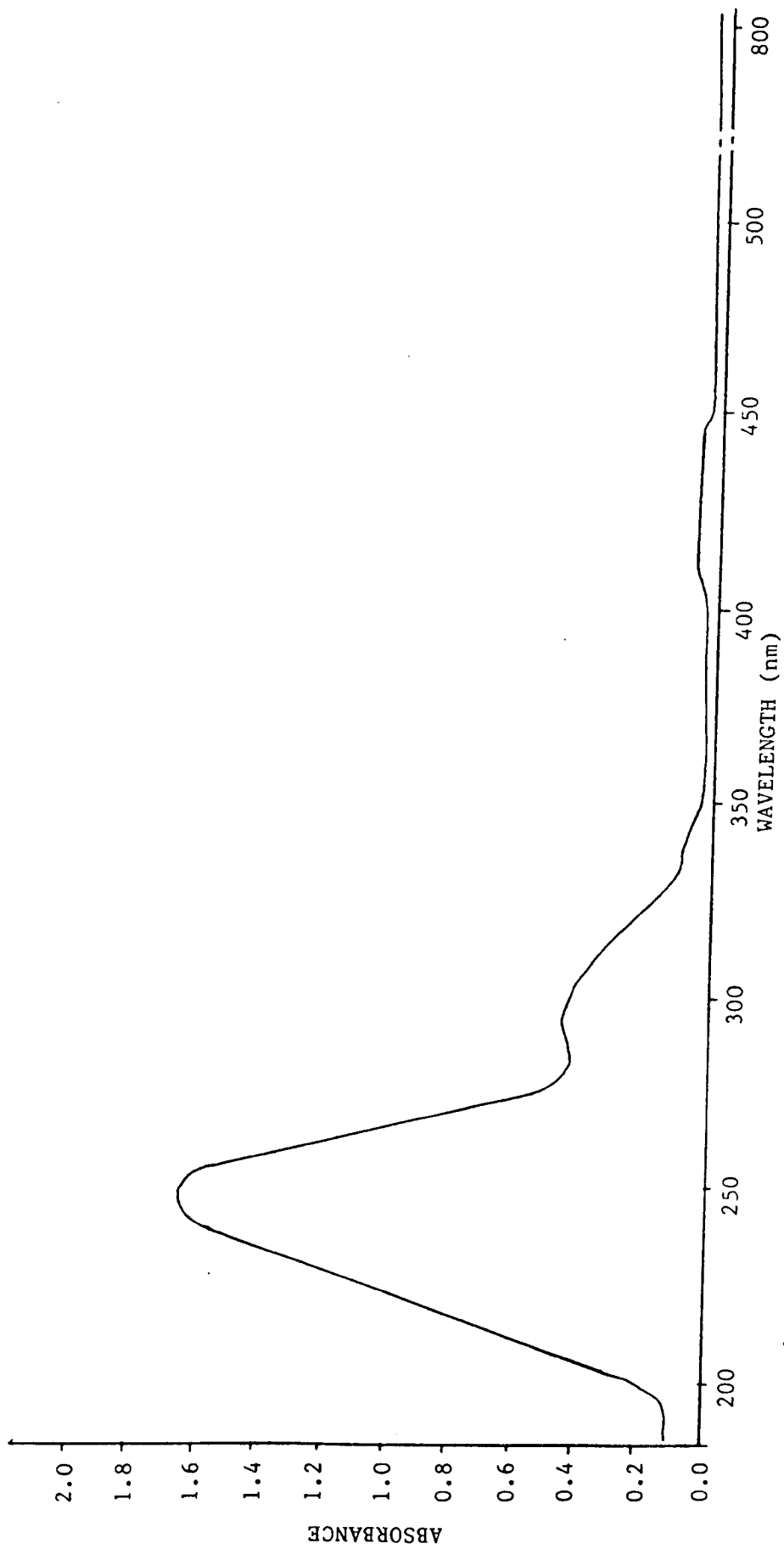
$$dI = -k I_0 \cdot db \qquad \text{Eqn. 16}$$

where  $dI$  is the change in intensity, and,  $k$ , is the proportionality constant.



**FIGURE 40.** ABSORPTION SPECTRA OF OIL IN  
HEXANE (1% v/v) SOLUTION.

FIGURE 41. ULTRA-VIOLET/VISIBLE SPECTRUM OF OIL IN ACETIC-ACID/CHOROBENZENE SOLUTION.



The right hand side of the equation is negative because,  $I$ , becomes smaller as  $b$  becomes larger. Rearranging the above equation shows that the fraction of radiation absorbed is proportional to the thickness transversed:

$$\frac{dI}{I_0} = -k db \quad \text{Eqn. 17}$$

If  $I_0$  is the incident radiation when  $b = 0$ , the above equation can be integrated to give:

$$\int_{I_0}^I \frac{dI}{I} = -k \int_0^b db \quad \text{Eqn. 18}$$

which gives:

$$\ln \frac{I}{I_0} = -k b \quad \text{Eqn. 19}$$

$$\log \frac{I_0}{I} = \frac{-k b}{2.303}$$

This equation is the final form of Lambert's law. It is an exact law and applies to any homogeneous, non-scattering medium regardless whether it is a gas, liquid or solid. The proportionality constant,  $k$ , depends on the temperature, pressure, wavelength and concentration of the system.

#### 3.4.2.2 Beer's Law.

This law deals with the effect of the intensity of radiation on the concentration of a solution of absorbing molecules in a transparent solvent. Beer found that increasing the concentration (of radiation absorbing solute in solution) had the same effect as a proportional increase in the radiation absorbing path (thickness). This means that the constant,  $k$ , in the Lambert law derivation above, is a function of solute concentration,  $C$ , :

$$\frac{k}{2.303} = a C \quad \text{Eqn. 20}$$

where,  $a$ , is a new proportionality constant, a characteristic for solute and wavelength

used.

Substituting the above equation into the final Lambert law equation:

$$\log I_0/I = a.b.C \quad \text{Eqn. 21}$$

The ratio  $I_0/I$  is called the transmittance,  $T$ , and is dimensionless. The left hand side of the above equation is a logarithm (pure number). The units of the terms on the right hand side must be dimensionally consistent:

- $a$  - absorptivity in litres per gram per cm,
- $b$  - the cell width in cm,
- $C$  - The concentration in grammes per litre.

In experimental work the terms % transmittance ( $\% T = I/I_0 \times 100$ ) and absorbance ( $A = \log I_0/I = 2 - \log \%T$ ) are used. Absorbance,  $A$ , is also known as optical density. The shortest form of Beer's law can be written as:

$$A = a.b.C \quad \text{Eqn. 22}$$

A graph of Absorbance against concentration is a straight line (of slope  $a.b$ ) through the origin as shown in Figure 42 below.

There are no known deviations of Lambert's law when applied to homogeneous solutions. Beer's law, however, shows deviations at high concentrations of some solutions due to changes in refractive index or optical density.

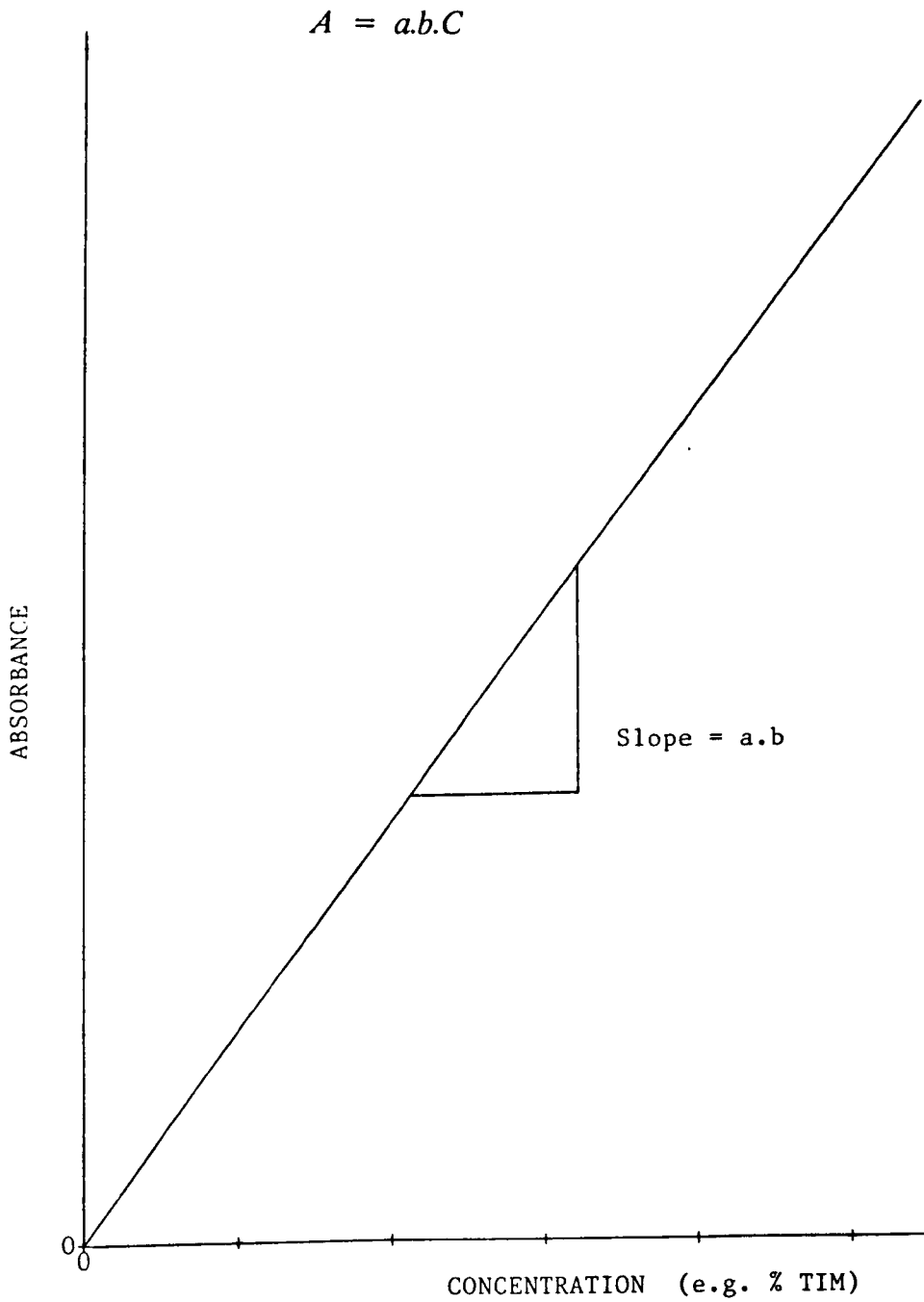
### 3.4.2.3 Limitations of Beer's Law.

In the derivation of Beer's law, the refractive index was assumed to be constant. The refractive index,  $n$ , has been observed [59] to vary with mixture concentration and is a function of true absorptivity:

$$a = \frac{n}{a_{\text{true}} (n + 2)^2} \quad \text{Eqn. 23}$$

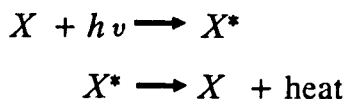
Beer's law is, therefore, limited to solutions that do not show significant variation in refractive index with changes in mixture concentration.

**FIGURE 42.** IDEAL BEER LAW PLOT OF ABSORBANCE VERSUS CONCENTRATION.



There are four assumptions implicit to the derivation of Beer's law:

1. The only mechanism of interaction between electromagnetic radiation and the solute is absorption. True absorption is defined by:

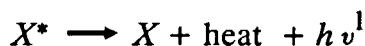


where  $h\nu$  - energy of incident radiation

$X$  - Ground state of absorbing particle

$X^*$  - Particle in excited state.

There are three other types of interaction which cause attenuation of radiation, namely, resonance emission, fluorescence (or phosphorescence) and scattering. Resonance emission is a rare phenomenon and is not discussed here (see [37] for further details). Fluorescence results in the emission of radiation of lower energy than that initially absorbed:



where  $h\nu^1$  - radiation of lower energy than  $h\nu$ .

The radiation,  $h\nu^1$ , is emitted in all directions and causes the apparent absorbance to be less than the true absorbance.

Scattering is the most likely source of deviation of the Beer law for the % TIM of used oils which contain large, solid, irregular shaped particles of many different sizes and type. The incident light will be scattered in all directions resulting in higher than expected absorbance measurements.

2. Only monochromatic radiation is used. Monochromatic radiation is assumed in the derivation of both Beer's and Lambert's Laws. Spectrometers pass a band or range of wavelengths through the sample cell and the narrowness of the band depends on the instrument specification and the nature of the test being conducted. Provided that the same cells, instrument and procedures are used, the errors arising from differences in instrumentation will be minimal.
3. For Beer's law to be followed, all absorbing species must act independently of one another regardless of number or kind. Interactions between absorption centres will have the effect of changing the energy requirements for absorption due to changes in quantum levels. As a result, absorption peaks may be altered in shape, position and intensity as the concentration varies. Therefore, for the Beer's Law based % TIM determination, the part of the absorption spectrum where absorbance does not vary over a range of wavelengths would be preferred. Absorbances for each component of mixtures are additive provided they are independent of each other:

$$A_{\text{total}} = a_1 b_1 C_1 + \dots + a_n b_n C_n = b \sum a_i C_i. \quad \text{Eqn. 24}$$

4. If the absorption cross-section of the specimen solution is not uniform, then deviations of Beer's law will occur due to the above factors as well as that of the exit beam of radiation being misaligned from the detector.

#### 3.4.2.4 Experimental.

Used oil samples of known % TIM (ex British Rail) were homogenised using a high speed vortex stirrer-vibrator. Oil solutions (3% m/m) in acetic acid:chlorobenzene (1:2, v/v) mixture were prepared in 50 ml conical flasks. Reference and sample solutions were placed in matched 10 mm silica cells of 1 mm path length, previously cleaned with Genklene and dried. A Perkin- Elmer uv-vis spectrometer was set up to measure the absorption spectrum in the 400 to 850 nm range, first for the solvents only (to 'zero' the machine) and then for the samples. Each sample was prepared just before use and all glassware was thoroughly cleaned and dried after use. The absorbance at 650 nm was noted from the spectra and plotted against % TIM.

During the preparation of the diluted oil samples it was noted that some of the oil samples would not dissolve or remain homogeneous for more than a few minutes. These samples had to be prepared and used as quickly as possible.

#### 3.4.2.5 Results.

The results of a number of different oils of known % TIM (by spot test, ex British Rail and Burmah Castrol by IP 316) is given in Table 30, below. The results indicate the dependence of % TIM on oil type and method of determination. The % TIM of the IP 316 based results by Burmah Castrol, show a discontinuity of linear behaviour when compared with British Rail 'spot' method, Figures 43 and 44.



**TABLE 30. CORRELATION OF % TIM BY DIFFERENT METHODS.**

Oil	Sample Number	% Total Insoluble Matter		
		IP 316	BR Spot method SAE 40    20W50	Absorbance (650 nm)
Dynamax	New			0.03
	1A	0.58	0.80    1.00	0.39
	1B	1.61	1.40    1.90	0.49
	1C	2.80	2.50    3.20	0.89
	1D	1.82	1.60    2.00	0.98
	1E	1.44	0.90    1.10	2.03
220 MXD	New			0.05
	2A	2.18	0.90    1.10	0.51
	2B	1.35	0.80    1.10	0.63
	2C	2.92	2.40    3.00	1.38
	2D	5.15	>3.00    >4.00	1.73
	2E	2.09	2.00    2.60	Off Scale

Note: All readings are within +/- 0.2. For sample 2D in Table 30, the spot test method gave over-range readings, hence the '>' sign is used before the value.

The results indicate that the more reliable % TIM values are those determined by the British Rail 'spot' method. The construction of the calibration graph could now be undertaken by diluting an oil sample of known high % TIM, to give samples of intermediate TIM values.

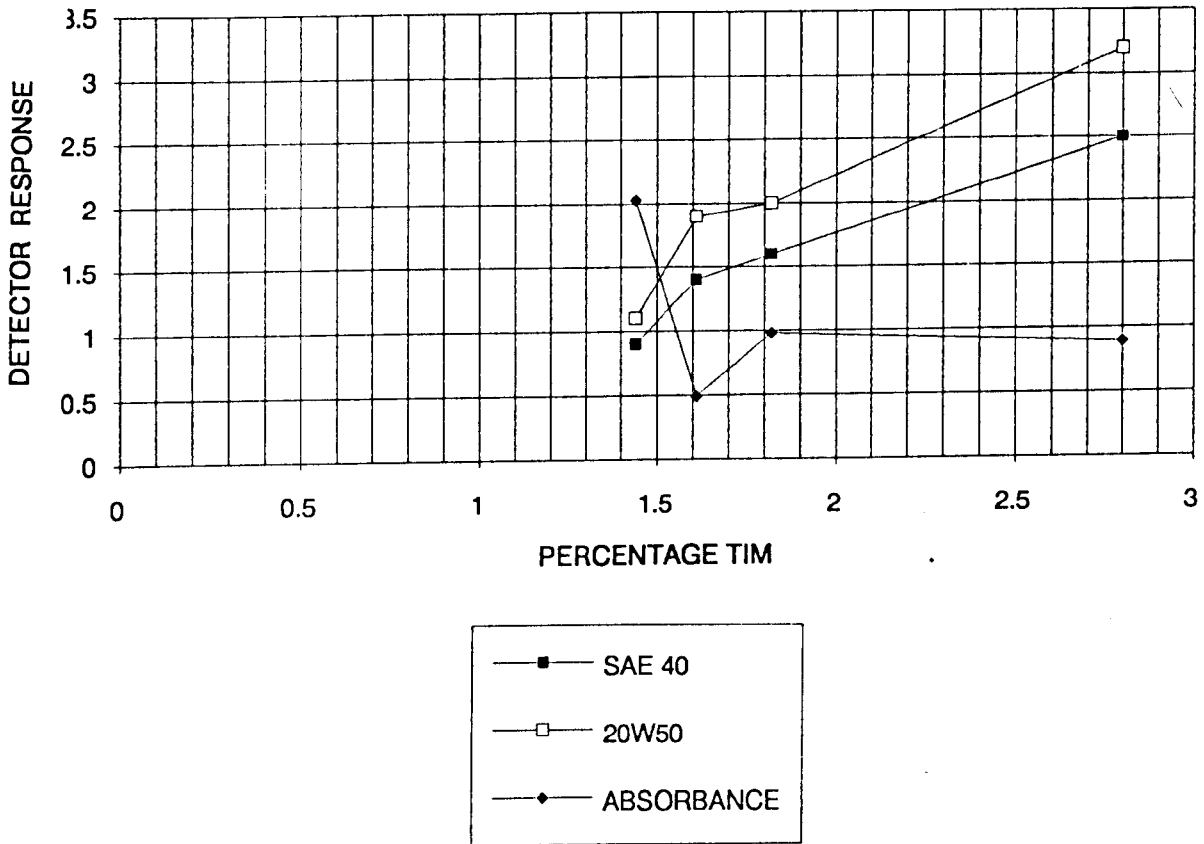
An oil sample of 2.91 % TIM (BR 'spot' method) was diluted with the same type of new oil (IL3030) to give a range of % TIM samples (see Table 31):

**TABLE 31. % TOTAL INSOLUBLE MATTER CALIBRATION MIXTURES.**

Theoretical value	BR 'Spot' value	Absorbance (650 nm)
0.00	0.00	0.02
0.25	0.35	0.16
0.50	0.62	0.33
0.50	0.62	0.33
1.00	1.09	0.57
1.25	1.35	0.72
1.50	1.44	0.83
1.75	1.69	0.91
2.00	2.09	1.09
2.25	2.16	1.24

**FIGURE 43.** PERCENTAGE TIM BY IP 316 AND BRITISH RAIL 'SPOT' TEST.

**DYNAMAX OIL**



**FIGURE 44.** PERCENTAGE TIM BY IP 316 AND BRITISH RAIL 'SPOT' TEST.

**220 MXD OIL**

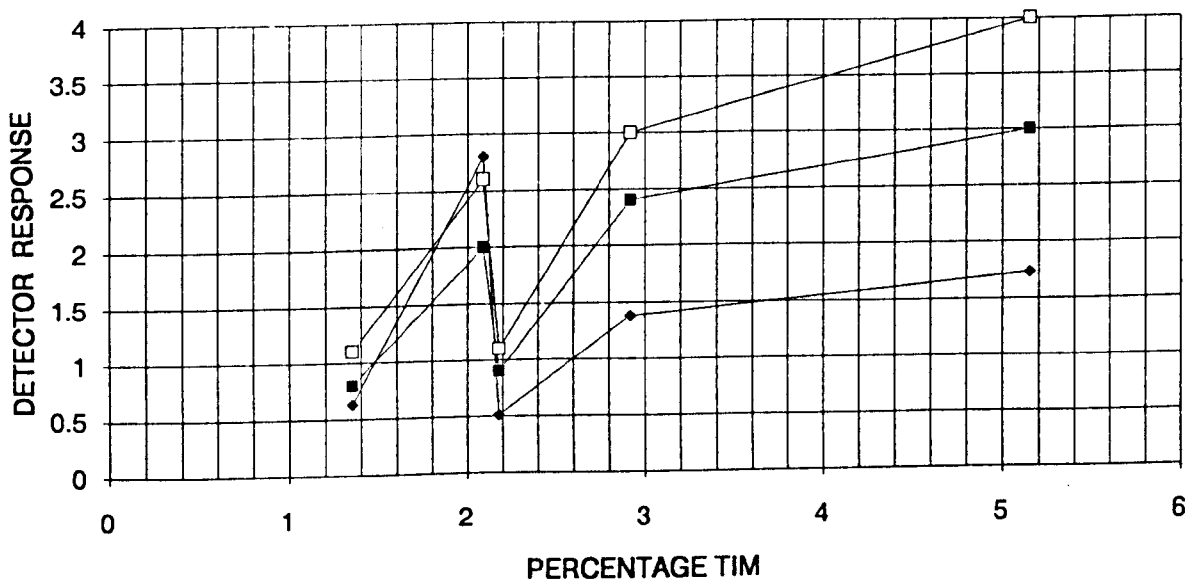
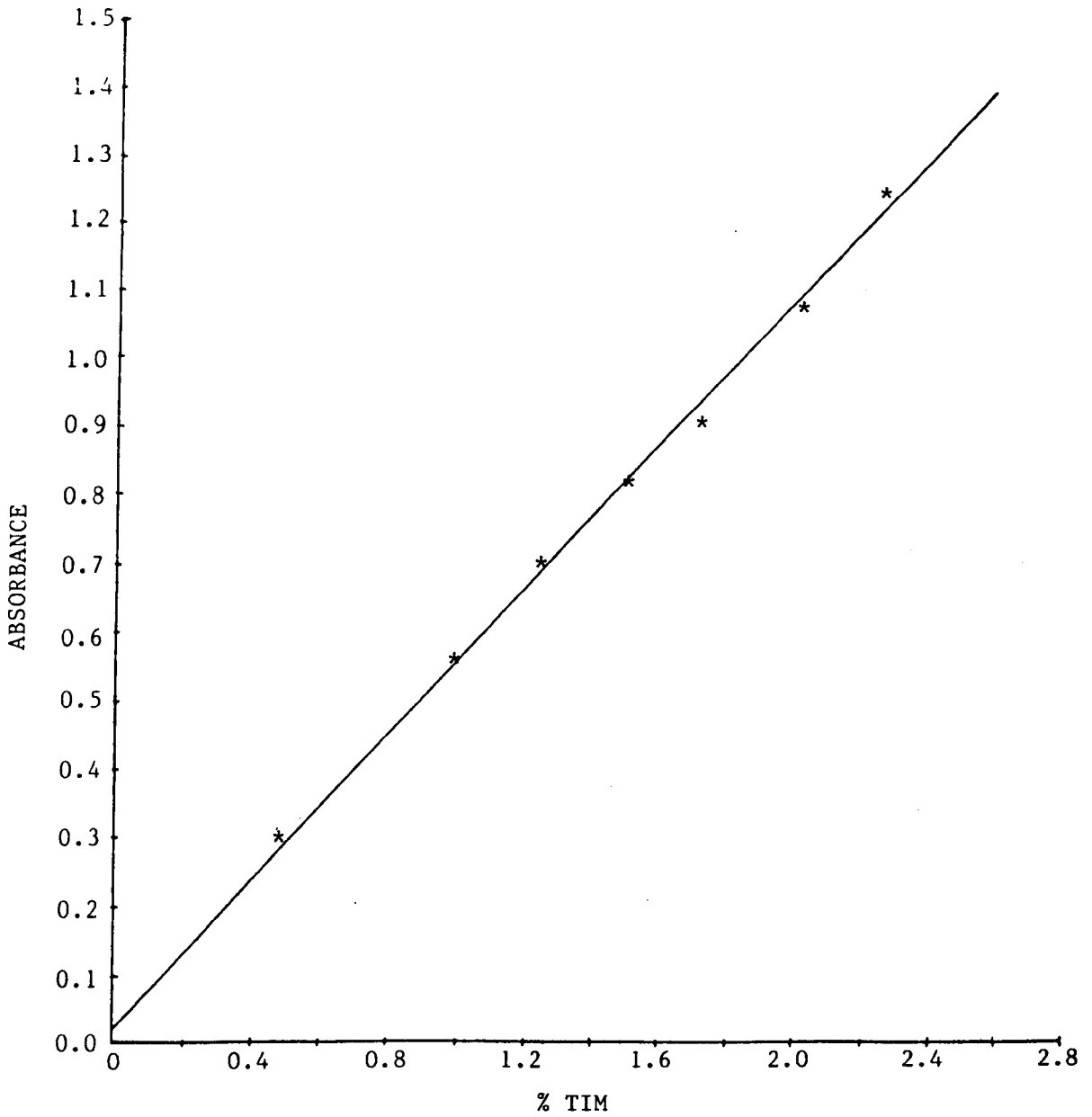


FIGURE 45. CALIBRATION GRAPH FOR PERCENTAGE TIM OF 1:30 OIL:HEXANE SOLUTIONS.



The above results are plotted in Figure 45, the absorbances were recorded at 650 nm for 3% oil (IL 3030) in solution mixtures. The graph shows that the results of the spot tests coincides with the absorbance data and that the Beer-Lambert law is followed. Further tests to determine the effect of oil type on the calibration graph was conducted, using two other oils (Dynamax and 220 MXD), showed no significant deviations on the original plot. Therefore, it can be concluded that the spectrometric absorbance method for the determination of percentage Total Insoluble Matter (% TIM) is independent of oil type provided that solution homogeneity is assured. The maximum absorbance of 2.0 limits the maximum % TIM (to about 3%) that could be measured on the spectrometer using a 3% oil solution. Therefore, by reducing the oil concentration by a factor of two, the range can be doubled to 6% TIM in order to meet the British Rail requirements. The lower concentration samples would still follow the Beer-Lambert law.

The 220 MXD based oil samples were used to check the validity of the higher % TIM samples at lower oil concentrations. Figure 46 shows the results of this check to be as expected. The % TIM for the oil sample 2D were found to be 4.3% (SAE 40) and 5.7% (SAE 20W50) which fits the originally observed over-ranged readings.

#### 3.4.3. Conclusion.

The ultra-violet/visible spectrometer is suitable for the determination of Total Insoluble Matter in the 450 nm to 800 nm wavelength range. The method follows the Beer-Lambert law for up to 6 % TIM based on a 1.0 mm path length cell and 1.5 % oil solution. The method gives data which agrees with the 'spot' test currently in use at British Rail and does not suffer from the sedimentation inconsistency experienced by the IP 316 method. This repeatable method is easily automatable for handling one sample per minute.

#### 3.4.4 Automation of TIM Determination.

A suitable, simple, monochromatic light source and detector system has been devised to fit at the outlet side of the TBN determination reaction vessel, Figure 20. The % TIM of the well stirred mixture is measured when the mixture is flushed out of the reactor at the end of the TBN determination. The advantage of this method of installation is that no additional sampling handling or any other operation needs to be unnecessarily duplicated. A schematic diagram of the circuit is shown in Figure 47.

### 3.5 CONCLUSIONS (for Chapter 3).

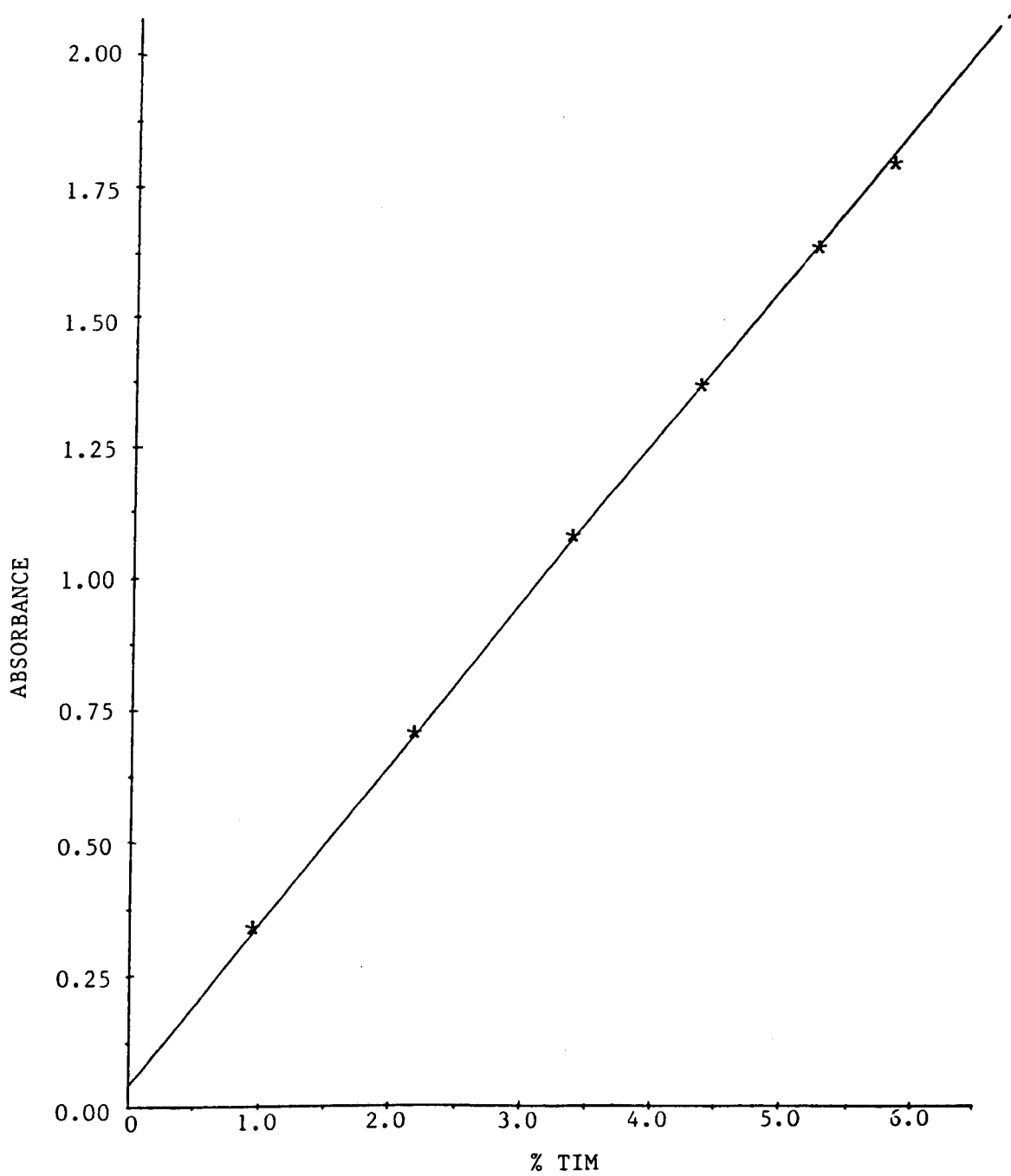
Three new and improved oil analyses methods have been developed during the course of this work, namely, Total Base Number (for both IP 177 and IP 276), Total Insoluble Matter and Water Content.

These new methods have been shown to work well for new formulated oils but more importantly, for used or severely abused oils as well.

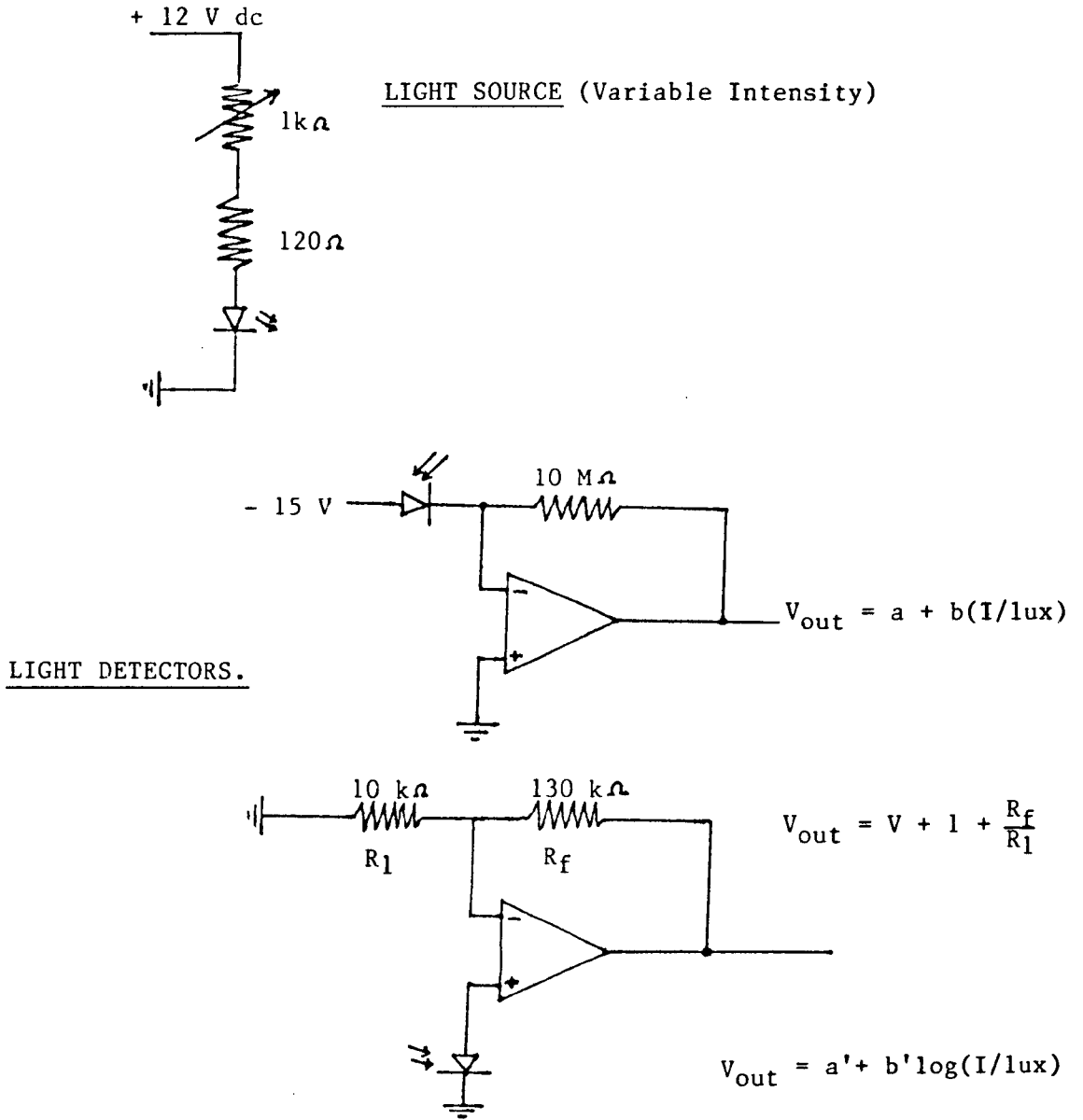
The basic, proven systems has been shown to have excellent repeatability and reproducibility and further development is required to fine tune these systems for quality assurance usage/automation.

Other potential methods have been extensively examined but the three analysis methods chosen are superior.

**FIGURE 46.** CALIBRATION GRAPH FOR PERCENTAGE TIM OF 1:60 OIL:HEXANE SOLUTIONS.



**FIGURE 47.** CIRCUIT DIAGRAM FOR PERCENTAGE TOTAL INSOLUBLE MATTER DETERMINATION APPARATUS.



For the photodiode:  $i \propto I/lux$   
 or  $V_{AC} \propto \log(I/lux)$

For the device used:  $V_{AC} = 0.180 + 0.07 \log_{10}(I/lux)$

The specified values of  $R_f$  and  $R_1$  are chosen to give

$$\Delta V_{AC} = 1V/decade$$

## CHAPTER 4.

### 4. ENGINE TESTING.

Engine operational life has been modelled successfully for a gas fuelled reciprocating internal combustion engine by Hassaan [35]. Hassaan's work was based on both the mechanical wear (rate), blowby and performance of the engine, and also on the contamination and deterioration of the lubricating oil. It was concluded that the engine's service life was more of a function of cylinder liner wear limits rather than that of any other engine part. Hassaan's work overlooked the wearing out of another critical component - the lubricating oil itself. Although derating an engine from its designed full power can prolong engine life, the use of a poorly suited or poor quality oil can nullify any such gains. Therefore, in order to model or predict the ultimate life of any engine, the engine wear must be considered in parallel with the lubricating oil life.

This work was undertaken to determine the ultimate life of a lubricating oil as well as that of a single cylinder, air cooled, diesel engine. The oil degradation was to be determined by a number of chemical and physical tests on the used oil. The engine life was to be followed by wear measurement of components by original and traditional techniques. The engine lubricating oil consumption was to be monitored regularly and samples of the used oil taken for analysis. The form that the engine wear or oil deterioration would take could not be known in advance under the operating conditions adopted, see below.

The experiment was set up by running two similar engines, under the same conditions but one of the engines, namely engine E2, was to receive regular servicing and oil changes whilst the other engine was to receive only oil top-up, namely engine E3. The former, serviced engine is the control for the latter engine which was expected to yield data on oil life as well as mechanical wear rates. In order not to have prolonged testing times, the engines were to be operated at the peak power (1.2 kW) speed of 3000 revolutions per minute.

The engine liner, piston, piston rings, valve stems and valve clearances were measured at regular intervals. The engines were run for 10 hour periods after which the sump oil was drained (overnight) and reused after weighing. Any oil shortage in the sump was made up with a measured quantity of fresh oil. The lubricating oil used was a military reference oil (OMD 75 specification) designated ER5D, a 10W30 oil. The engines were run on a military reference diesel fuel containing 1% sulphur. Oil samples (10g) were taken during the drain down period.



#### 4.1 ENGINE MONITORING.

In order to continuously monitor the two diesel engines and to periodically take measurements of engine temperatures and pressures, a computer system and control hardware was developed. The control hardware developed included frequent checking of various temperatures and pressures, if any of which exceed a given operating range, would result in immediate shut-off of the engine. The parameter which results in a shut-off condition is high-lighted along with the time of occurrence and the value of that parameter. The engines could be shut-down automatically on a fixed time basis if required. Each of the two engines was monitored either separately or concurrently, by the same computer and they could started or stopped at different times, without affecting each other. The schematic diagram of the engine installation is shown in Figure 48. A photograph of the engines and equipment is shown in Figure 49. The circuitry of the eight input channels of the control (I/O) unit is shown in Figure 50. The computer programme used to monitor and control the two engines is given in Appendix D.

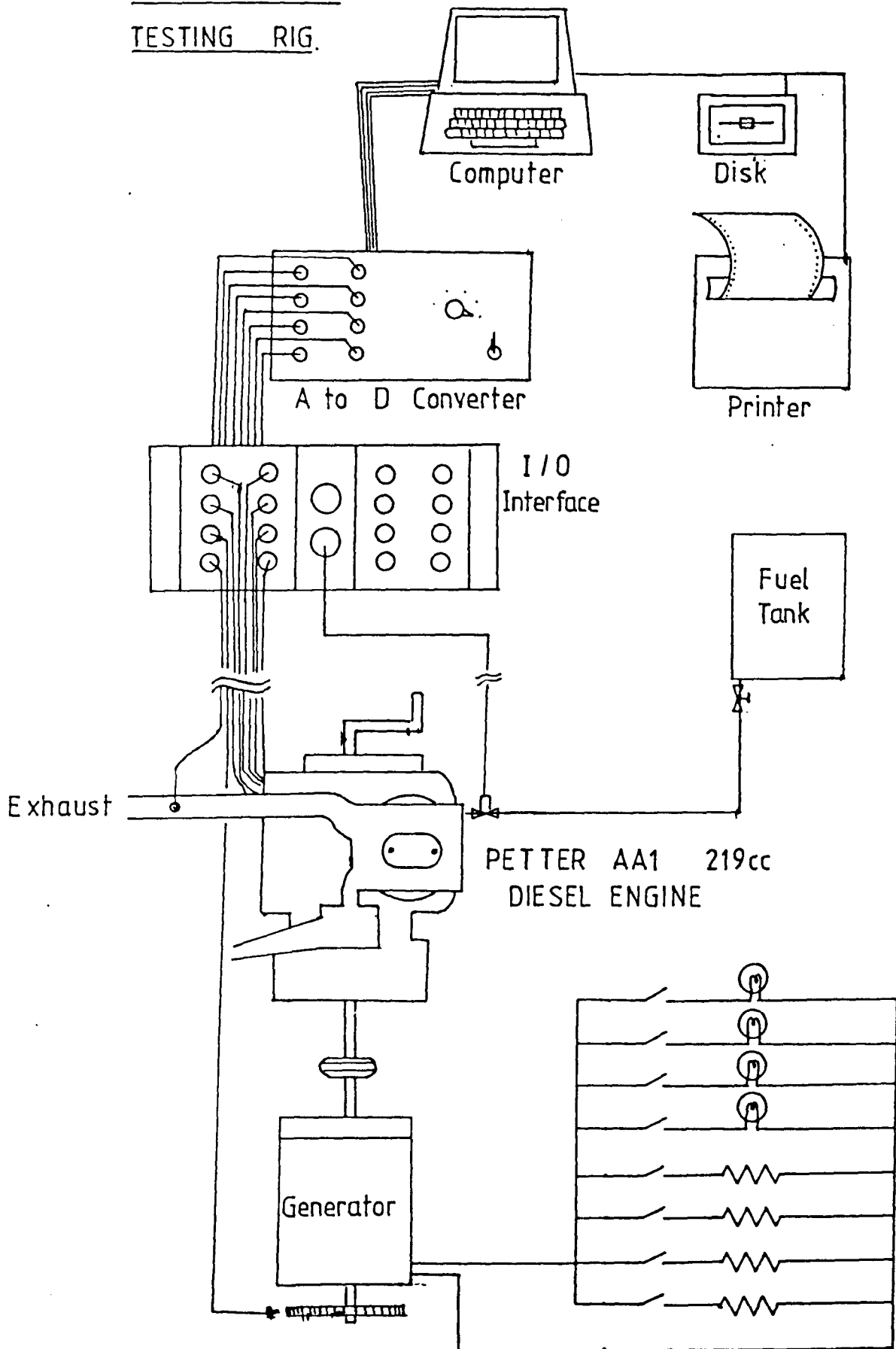
#### 4.2 ENGINE WEAR MEASUREMENT.

From the work carried out by Hassaan [35], it was concluded that the cylinder liner wear determined the ultimate life of an engine. It was, therefore, decided that the wear measurement of the diesel should be confined to the top-end reciprocating components. The engine was of simple design and had easy access to the cylinder liner, cylinder head and the piston. These components could be removed from the engine on the test-bed within a few minutes, without disturbing the crankshaft, camshaft, fuel injector or their timing positions. The only gasket that needed replacing on reassembly was the cylinder head gasket which made testing a cheap and easy exercise.

#### 4.3 CYLINDER BORE WEAR.

The cylinder liner inside diameter was measured at various points down the bore along the crankshaft axis and at an axis perpendicular to the crankshaft, using bore gauges and vernier calipers. A deep scratch was made on the bore using a diamond stylus at various positions in the bore liner, using the equipment shown in Figure 51. The cylinder liner was held in a lathe and turned slowly by hand to give a scratch of 10mm length. The depth of the scratch was measured periodically using a Talysurf or the portable Surftronic, see Figure 52.

ENGINE ROOM  
TESTING RIG.



**FIGURE 48.**  
ENGINE CONTROL SYSTEM.

**FIGURE 49.**

(a) 'MARKON' ELECTRIC DYNAMOMETER. ↓

(c) 1 AND 2 kW HEATER ELEMENTS ↓

(b) 'PETTER AA1' DIESEL ENGINE. ↓

(d) 100 W BULB BOARD WITH VOLTMETERS, AMMETERS AND SWITCHES. ↓

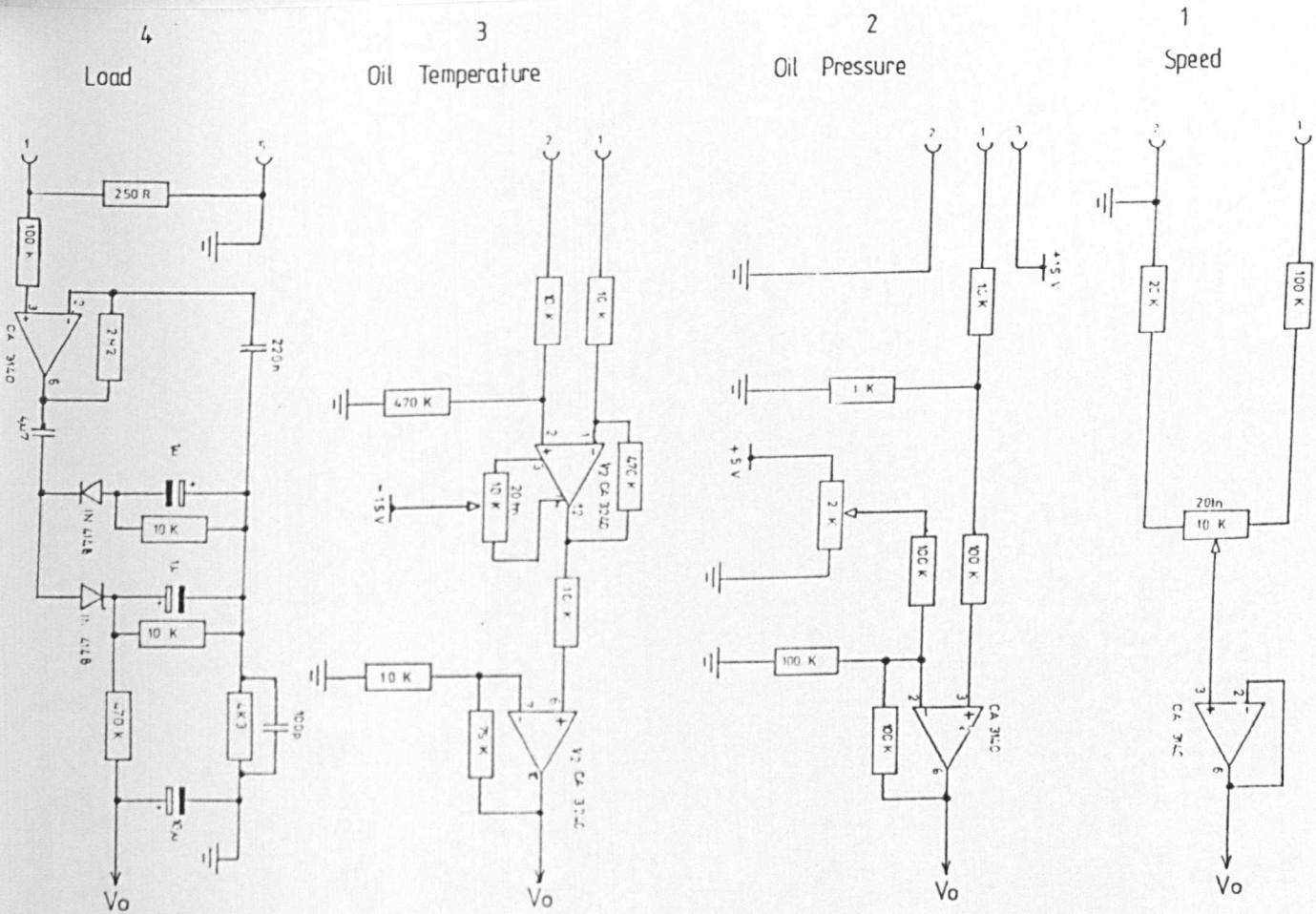


FIGURE 50. I/O CHANNEL (1-8) CIRCUITRY.

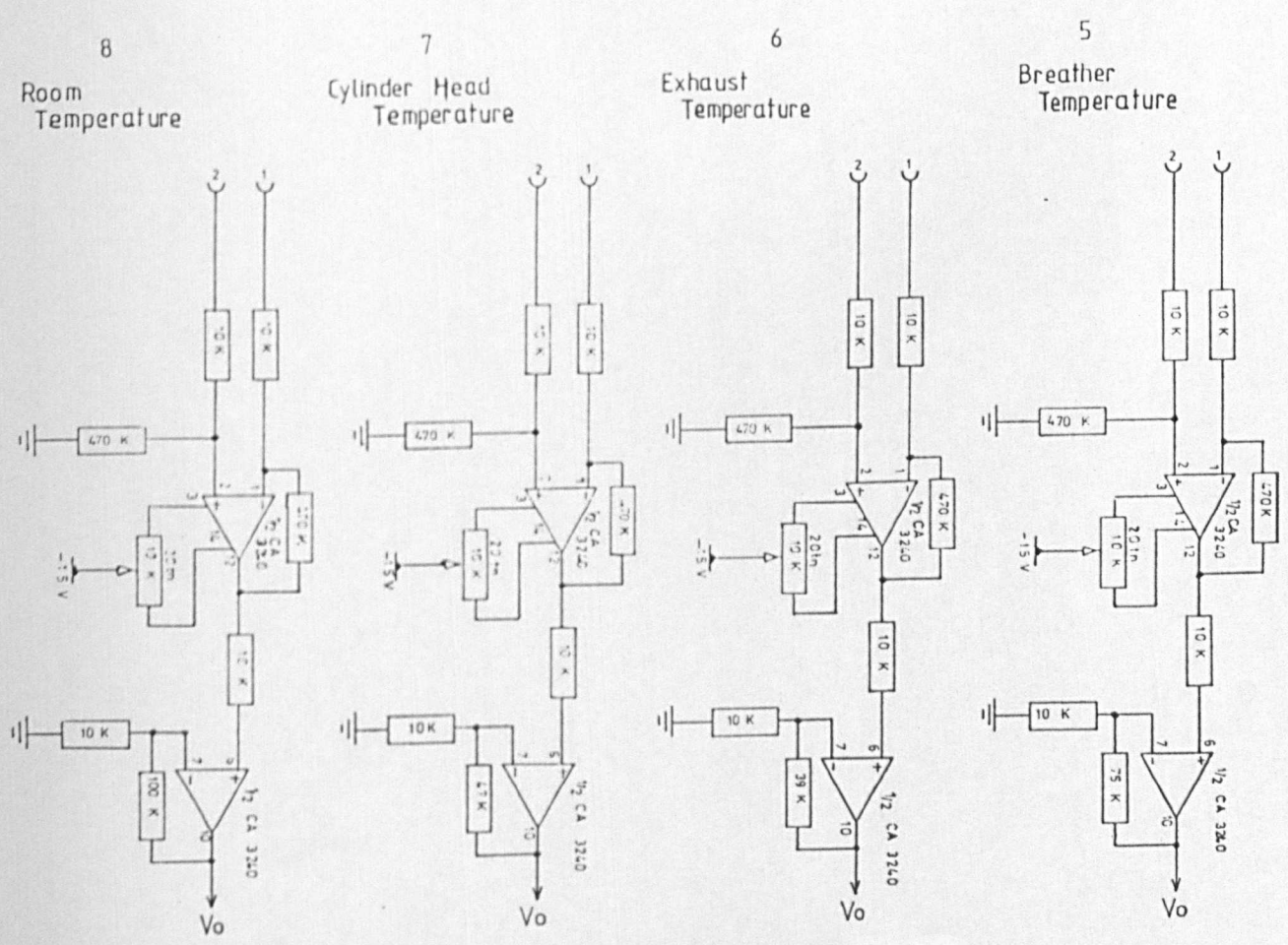
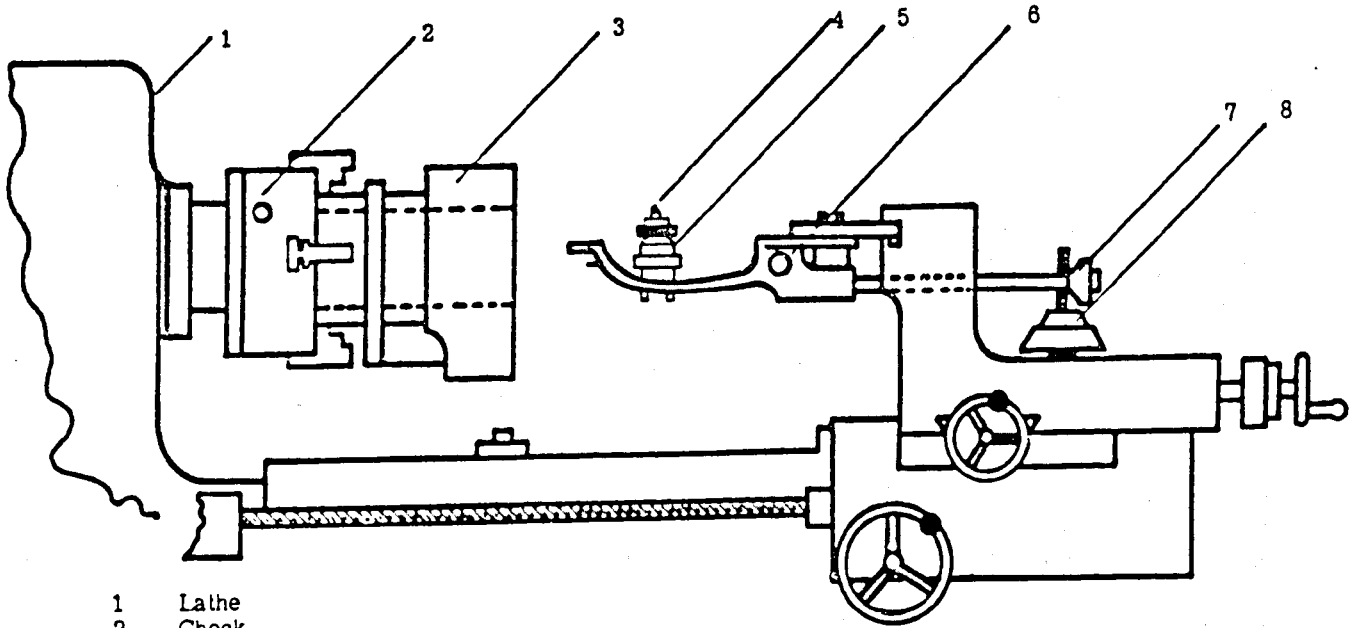
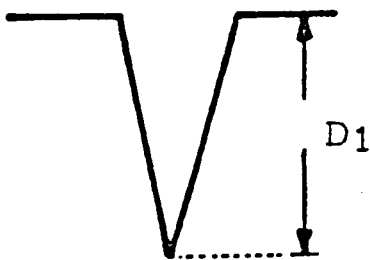


FIGURE 51. APPARATUS USED FOR MAKING DIAMOND CUT SCRATCH IN CYLINDER BORE (LINER).

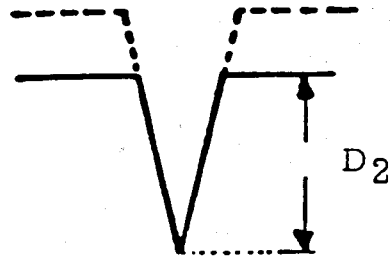


- 1 Lathe
- 2 Chock
- 3 Cylinder Engine Block
- 4 Pyramid Diamond
- 5 Diamond Holder
- 6 Apparatus Bearing
- 7 Counter Weight
- 8 Load

Schematic Drawing of the Scratching Apparatus



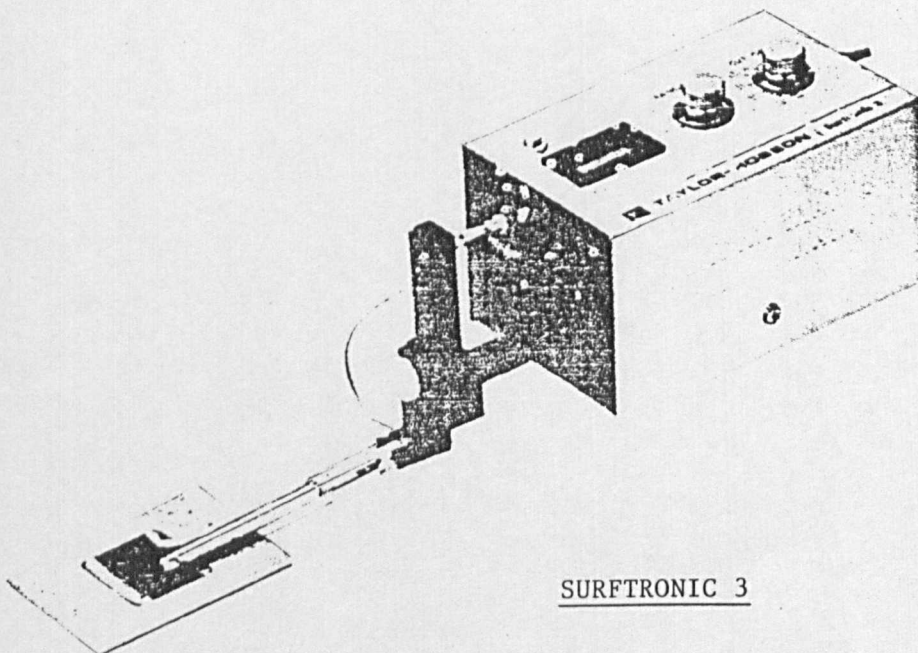
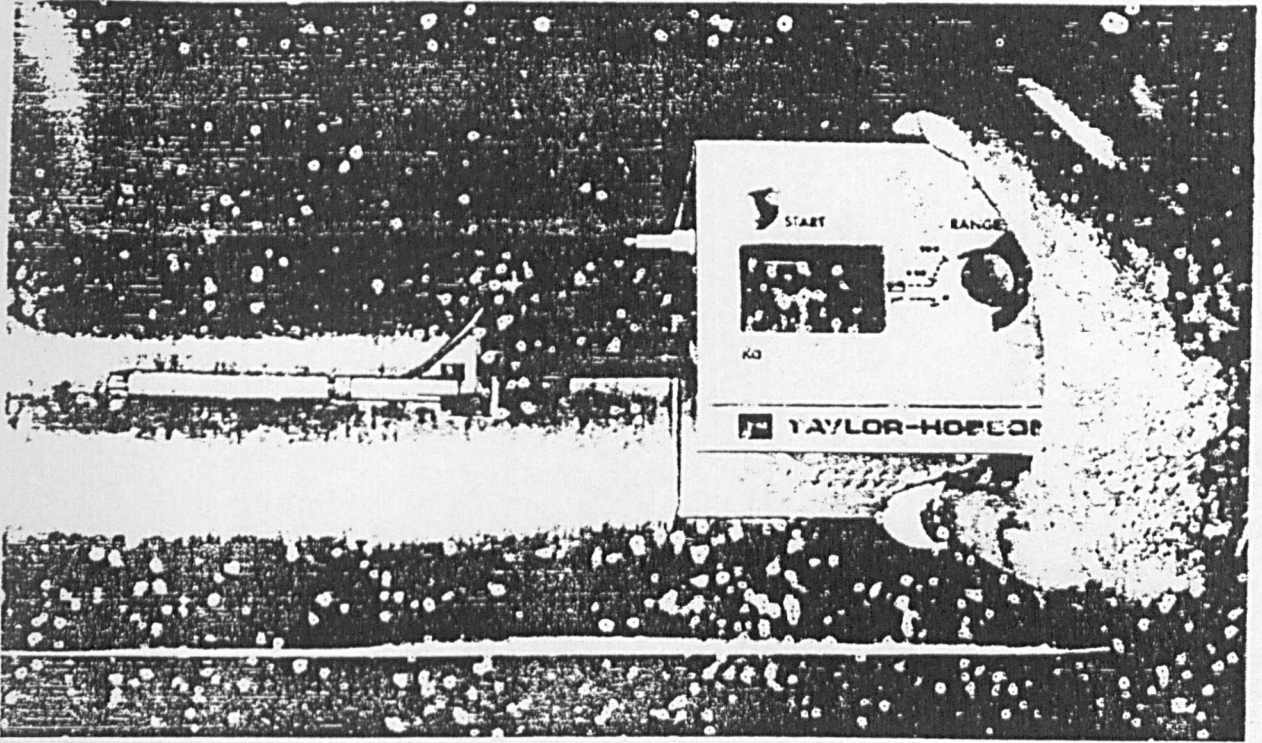
Scratching Mark Before Test



Scratching Mark After Test

$$\text{WEAR LOSS } \Delta D = D_1 - D_2$$

FIGURE 52. SURFTRONIC 3 - SCRATCH DEPTH MEASUREMENT APPARATUS.



SURFTRONIC 3

#### **4.4 PISTON, PISTON RING AND GROOVE WEAR.**

Due to the high pressures encountered in diesel engines, it was decided to determine the wear characteristics of the piston. Changes in colour underneath the piston crown could also be assessed whilst the piston was removed, to give an estimate of the temperatures experienced in that region. Wear measurement of the piston rings and ring-grooves can give information about performance losses, oil consumption and blowby flow rates.

#### **4.5 ASSESSMENT OF ENGINE CONDITION.**

The condition of the engines could be assessed from examination of the above measured components. The best indicator of engine condition was, however, not solely due to the condition of the liner wear factor, but equally, a function of oil consumption control. Liner wear, as shown by the removal of metal near the top of piston-ring travel area, was observed to increase with operational time. The unexpected polishing and scuffing of the liner resulted in premature loss of engine oil consumption control. This polishing of the cylinder liner is the result of the high (1%) sulphur content of the fuel, the poor oil quality and the operation of the engine at the designed maximum output. These characteristics determine the ultimate life of the engine and renewal of these components would be necessary to overhaul the engine.

#### **4.6 OIL CONSUMPTION.**

Loss of oil consumption control depends on the sealing efficiency of the piston rings, the smoothness (oil retention ability) of the liners and of the valve stem, valve guides and seals. These components determine the economically useful life of the engine provided that unexpected catastrophic main or big-end bearings failures do not occur first. Loss of oil consumption control can impair engine performance due to unacceptable oil levels and high oil consumption may result in legal and environmental infringements as well as the cost of frequently making up for the lost oil.

#### **4.7 OIL ANALYSIS.**

The oil samples generated by the diesel engine was analysed using both chemical and physical test methods. The physical tests included viscosity determination at 100 °F (37.8 °C) and at 210 °F (98.9 °C), oil blackness, oxidation (FTIR) and total insoluble matter determination. Chemical analysis of the oil included TAN, TBN, wear and additive elements (Ca, Zn, P, S, Na, Cr, Al, Pb, Fe, Cu, Ba, Si), viscosity index improver

degradation, oil oxidation and volatility.

## 4.8 RESULTS.

### 4.8.1 Engine Wear.

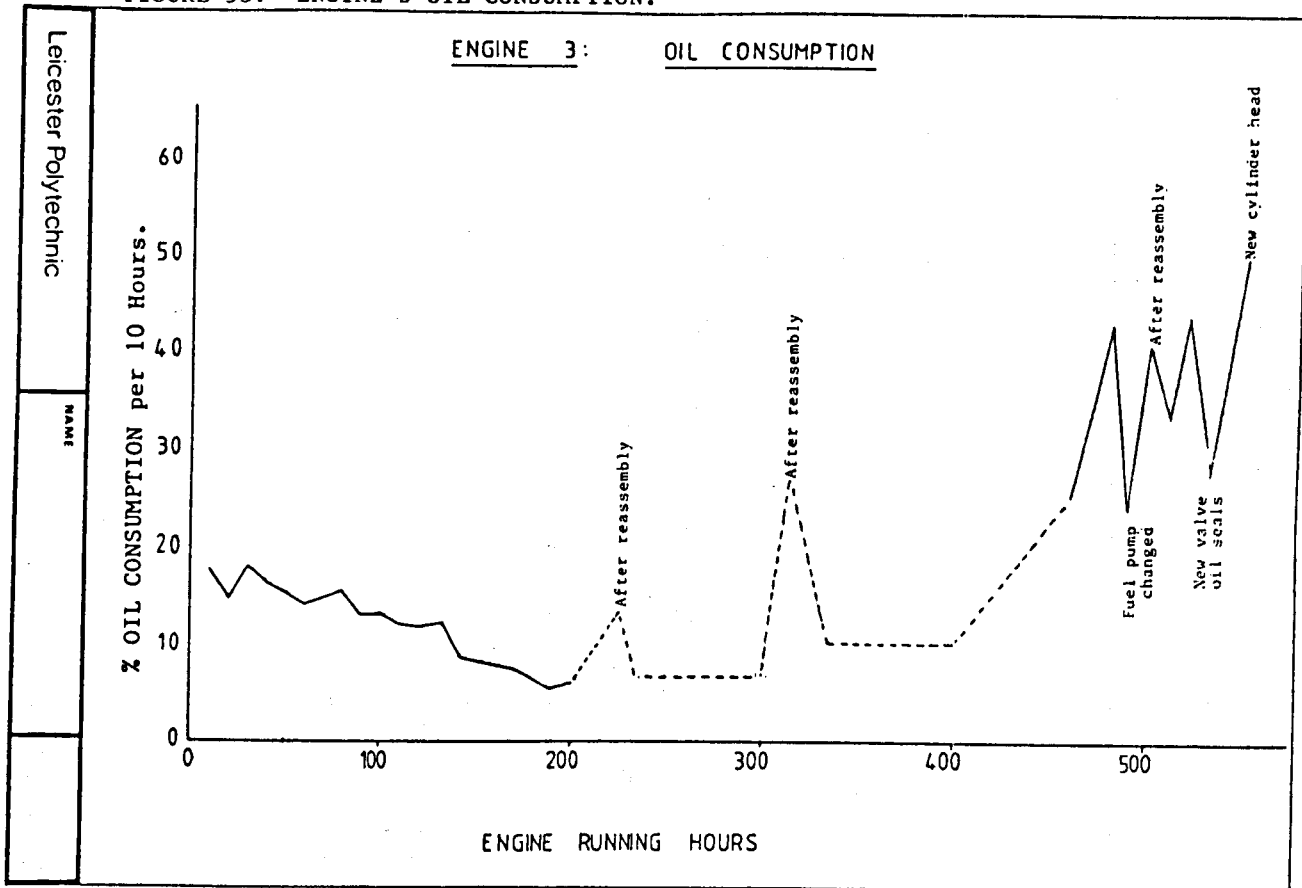
The engines (E2 and E3) initially consumed oil at a high rate at the beginning of the running-in. The oil consumption, measured as a percentage of oil charge of the sump and also as a percentage of the fuel consumption, gradually decreased during running-in and settled to a value lower than the 8% (per ten hours) level recommended by the engine manufacturer. After 350 hours of engine operation, the oil consumption of engine E3 began to increase steadily, up to 50% (per ten hours) at 550 hours, an unacceptably high level, Figures 53 and 54.

Various measures were taken to try to reduce the oil consumption of engine E3, Figure 55. In turn, it was thought that the oil was leaking down the valve stem as a result of increasing wear. Comparative measurements of the installed and new valve stems showed no evidence of excessive wear of the valve stems or the valve guides. A simple leak test comparison between the existing engine (E3) cylinder head and a new cylinder head showed an approximately doubled rate of leakage of the worn cylinder head when compared with that of the new cylinder head. Valve stem oil-seals were replaced on the existing cylinder head after which the oil consumption rate, per ten hours, initially decreased to 30% from 50% before increasing again. In turn, the cylinder head was replaced, then the piston and rings were replaced, all of these changes having only a small or temporary effect on oil consumption. The conclusion was that the cylinder bore had become 'polished' or 'glazed' in 550 hours running.

Table 32 and Figures 56 and 57 show the surface metrology analysis of the cylinder bore of Engine (3), for two positions, one sample trace obtained on the worn (top, thrust) side of the bore, the other on the originally machined, but unworn part of the bore, below the lowest travel limit of the piston. From the traces obtained and from the surface analysis parameters, it is clear that the bore is very much smoother after 550 hours than when it was originally installed, as shown by the unworn part of the bore. The diametral wear of the bore is shown in Figures 58 and 59. Moreover, the pattern of wear for the original set of piston and rings, Figures 60, 61 and 62, do not show any excessive wear (rates) and would, therefore, not be the cause of the considerably high oil consumption. It was concluded that the bore wear and smoothness was the cause of the excessive oil consumption after 550 hours running with only oil make-up, no oil changes being made.

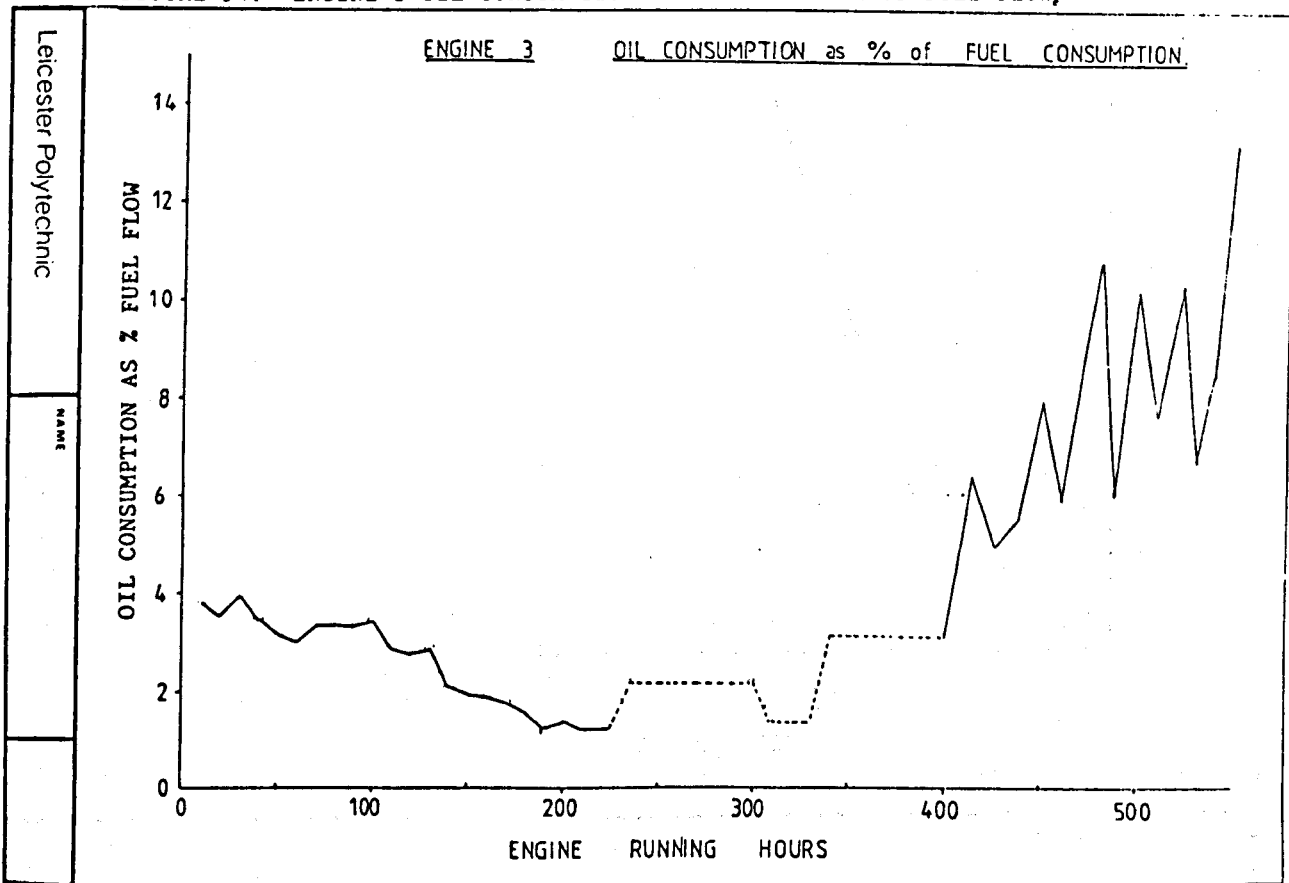


FIGURE 53. ENGINE 3 OIL CONSUMPTION.



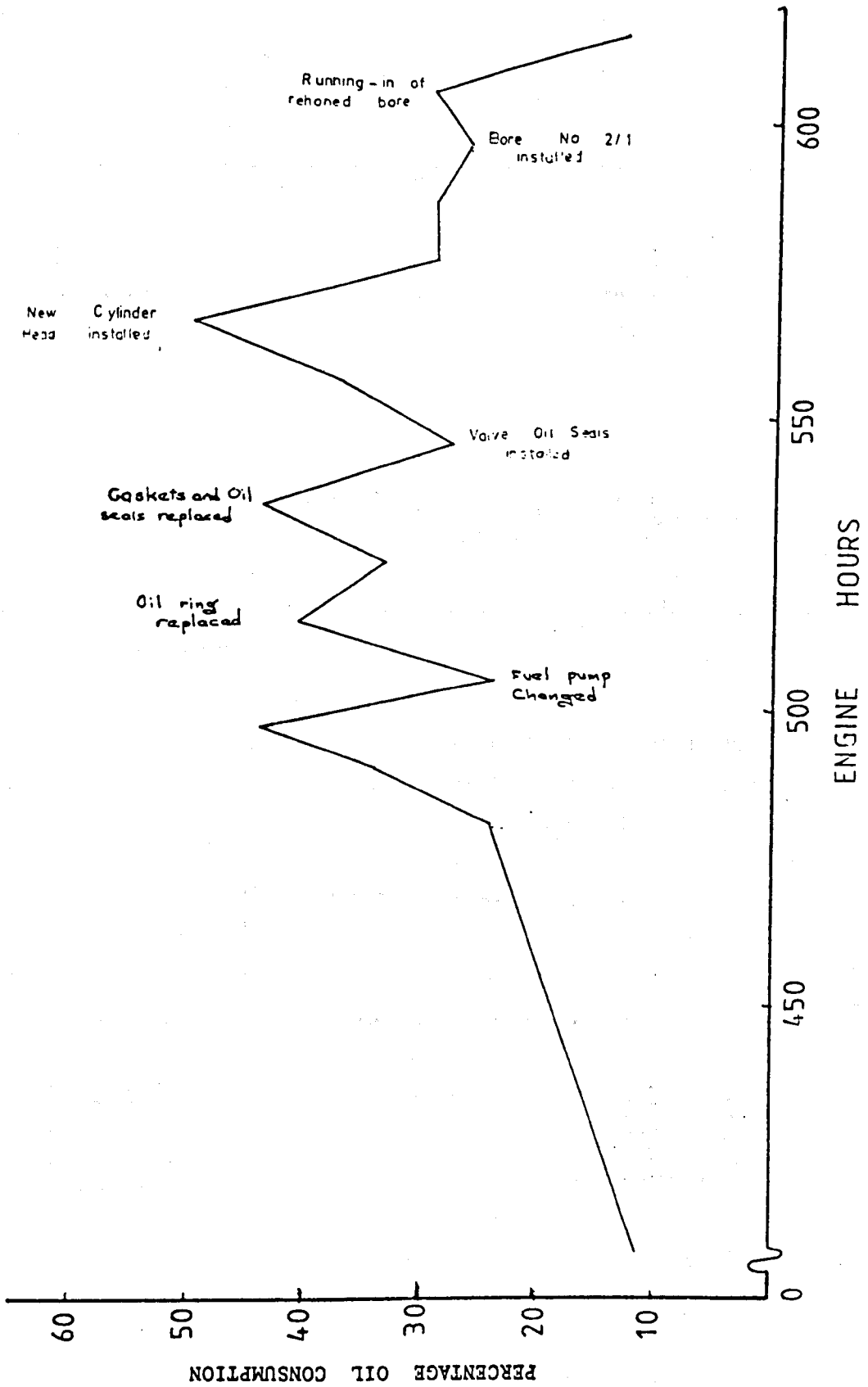
R56

FIGURE 54. ENGINE 3 OIL CONSUMPTION AS A PERCENTAGE OF FUEL FLOW.



R56

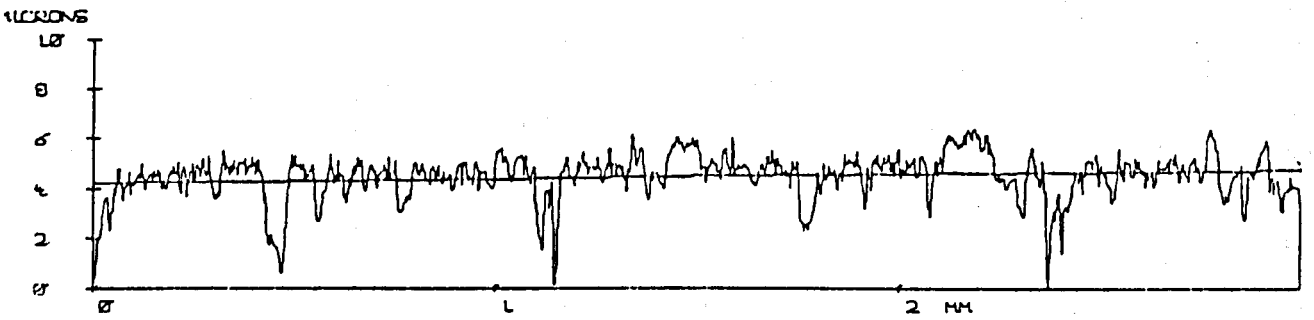
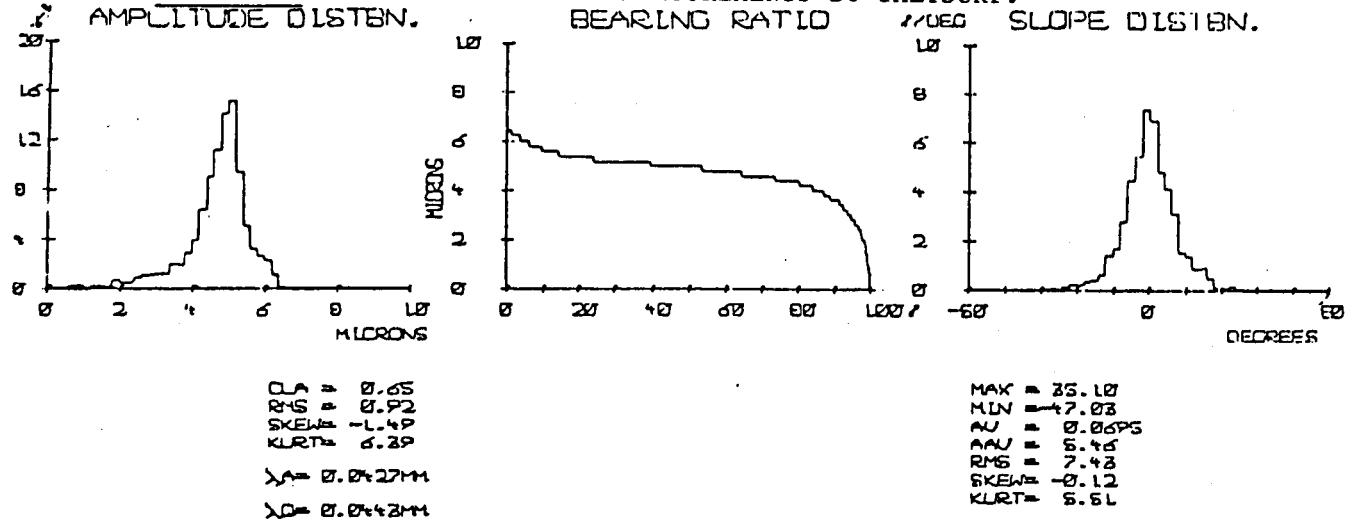
FIGURE 55. ENGINE 3: OIL CONSUMPTION



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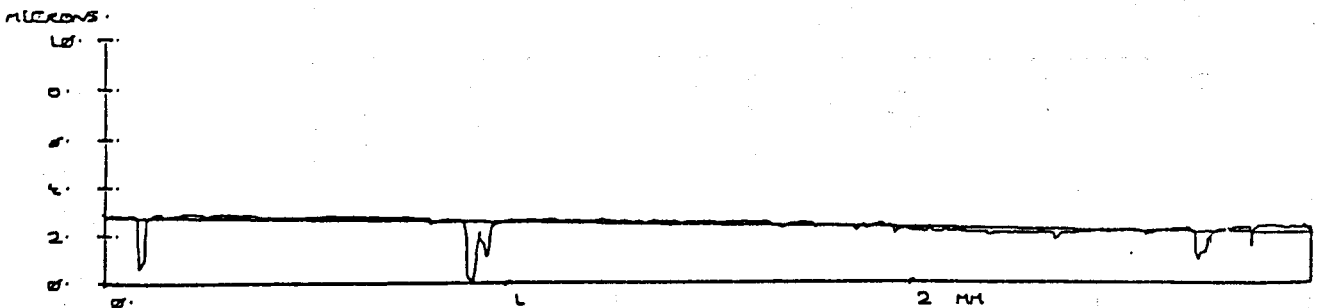
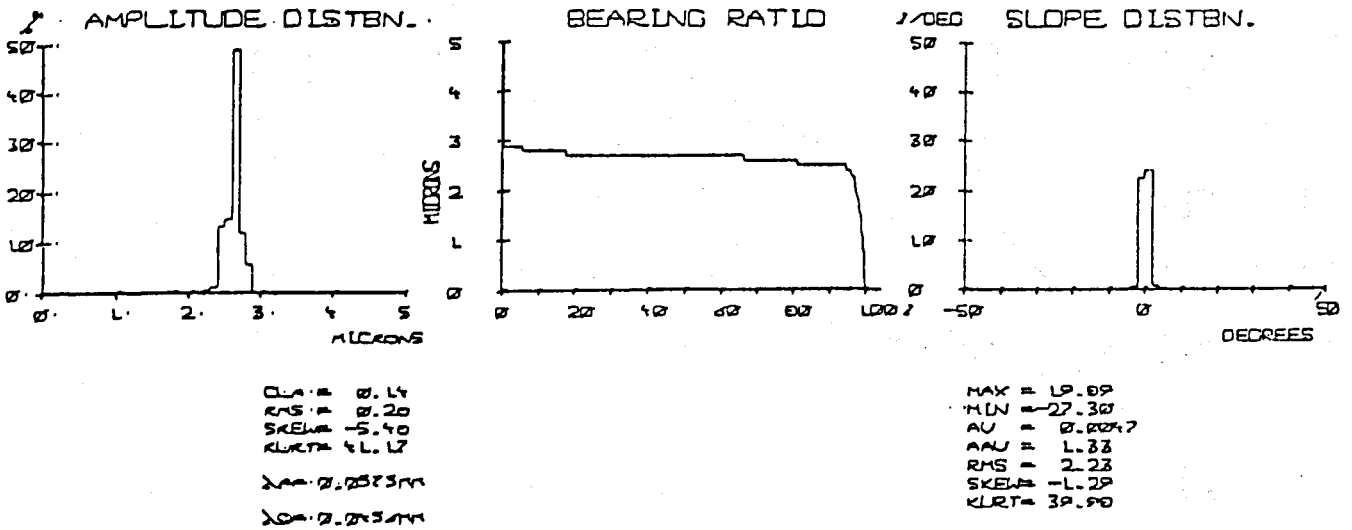
NAME

FIGURE 56. NEW BORE SURFACE MEASUREMENTS BY TALYSURF.



EST NO. 2/SK T M-SC 1500 SAMPLES AT 2 MICRONS

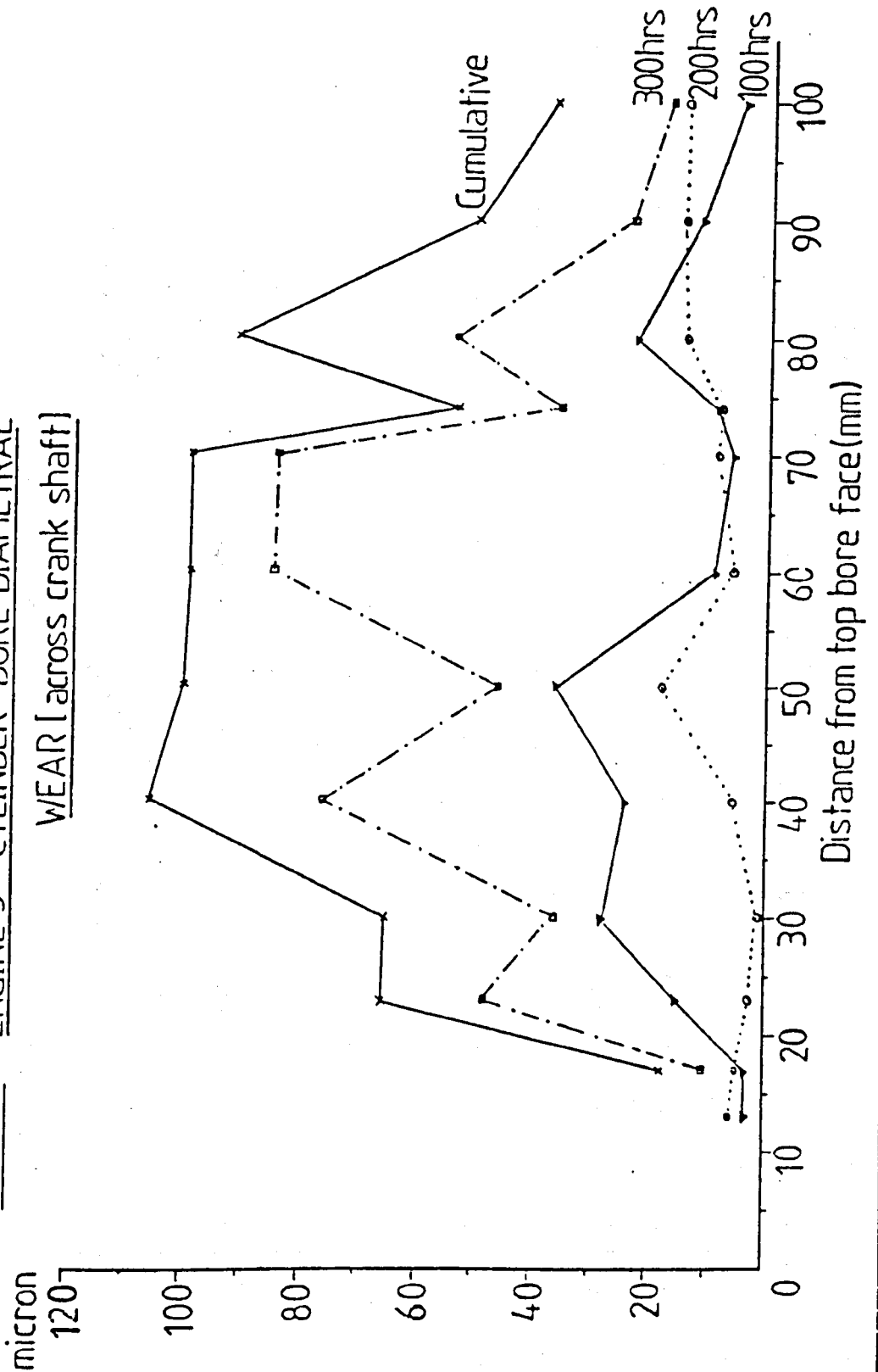
FIGURE 57. WORN BORE (550 Hours) SURFACE MEASUREMENTS BY TALYSURF.



TEST NO. 3/SK/350H/1/40 1500 SAMPLES AT 2 MICRONS

ENGINE 3 CYLINDER BORE DIAMETRAL WEAR [across crank shaft]

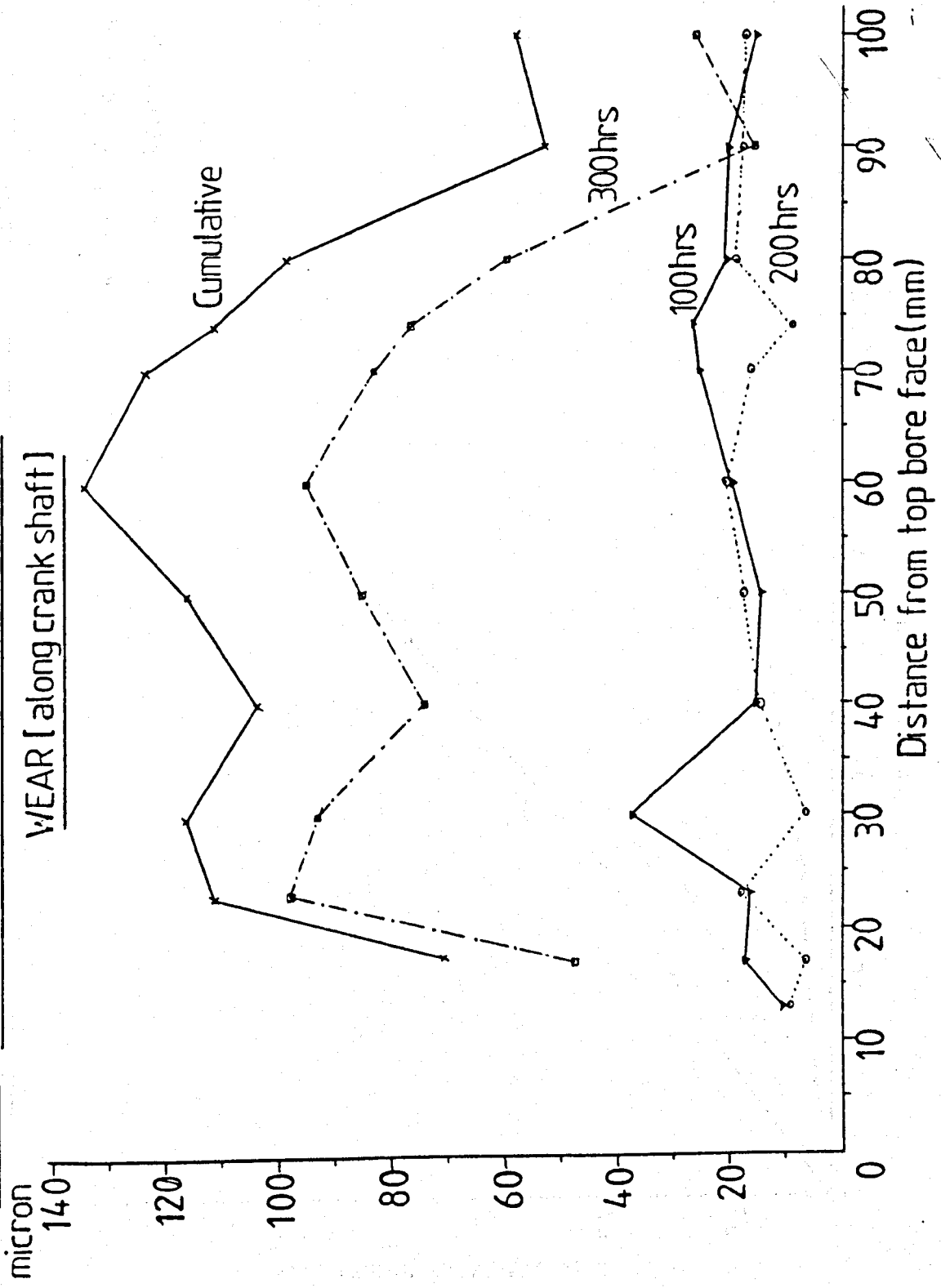
FIGURE 58.



**ENGINE 3 CYLINDER BORE DIAMETRAL**

**WEAR [ along crank shaft ]**

**FIGURE 59.**

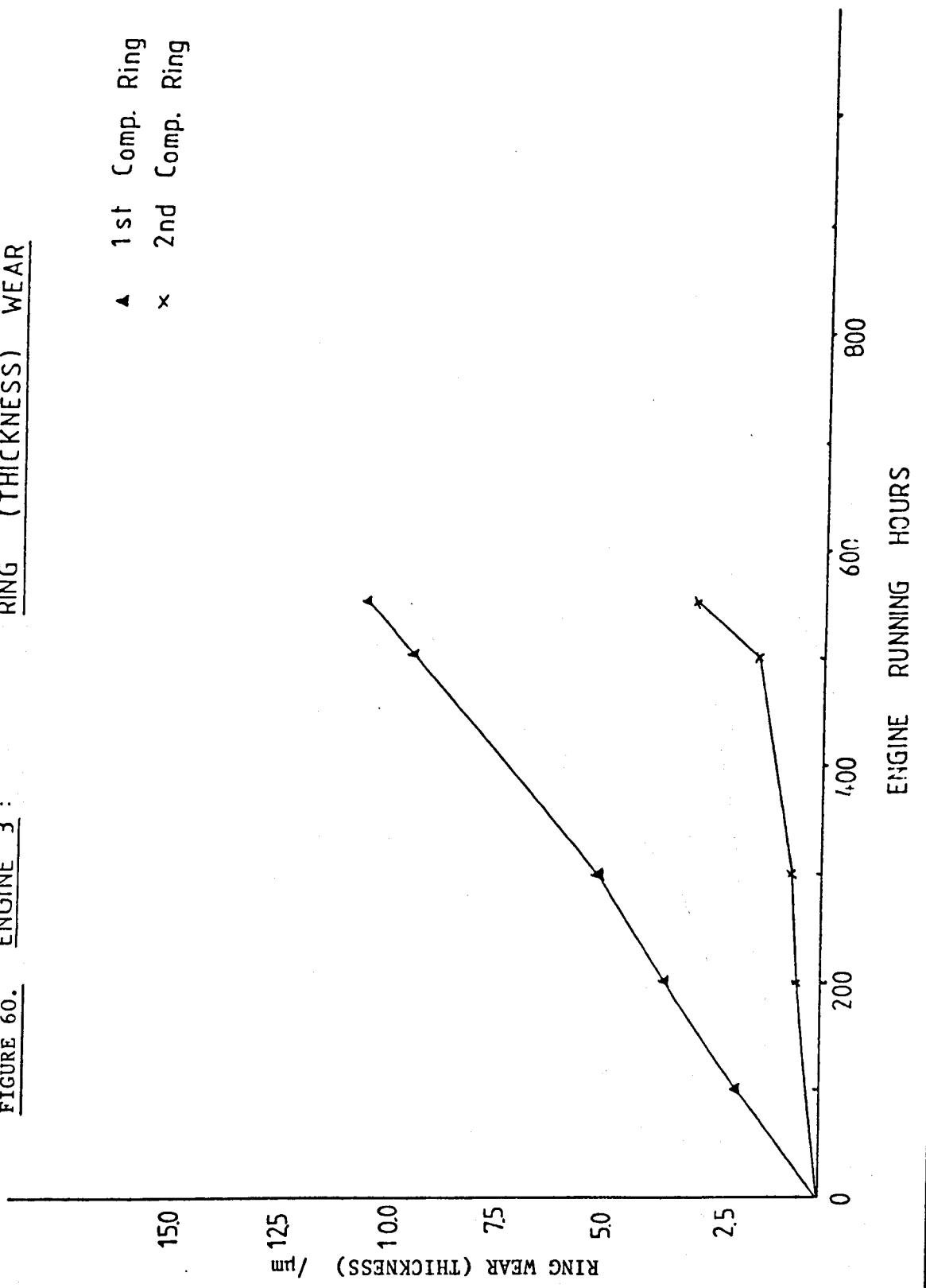


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FIGURE 60. ENGINE 3 : RING (THICKNESS) WEAR

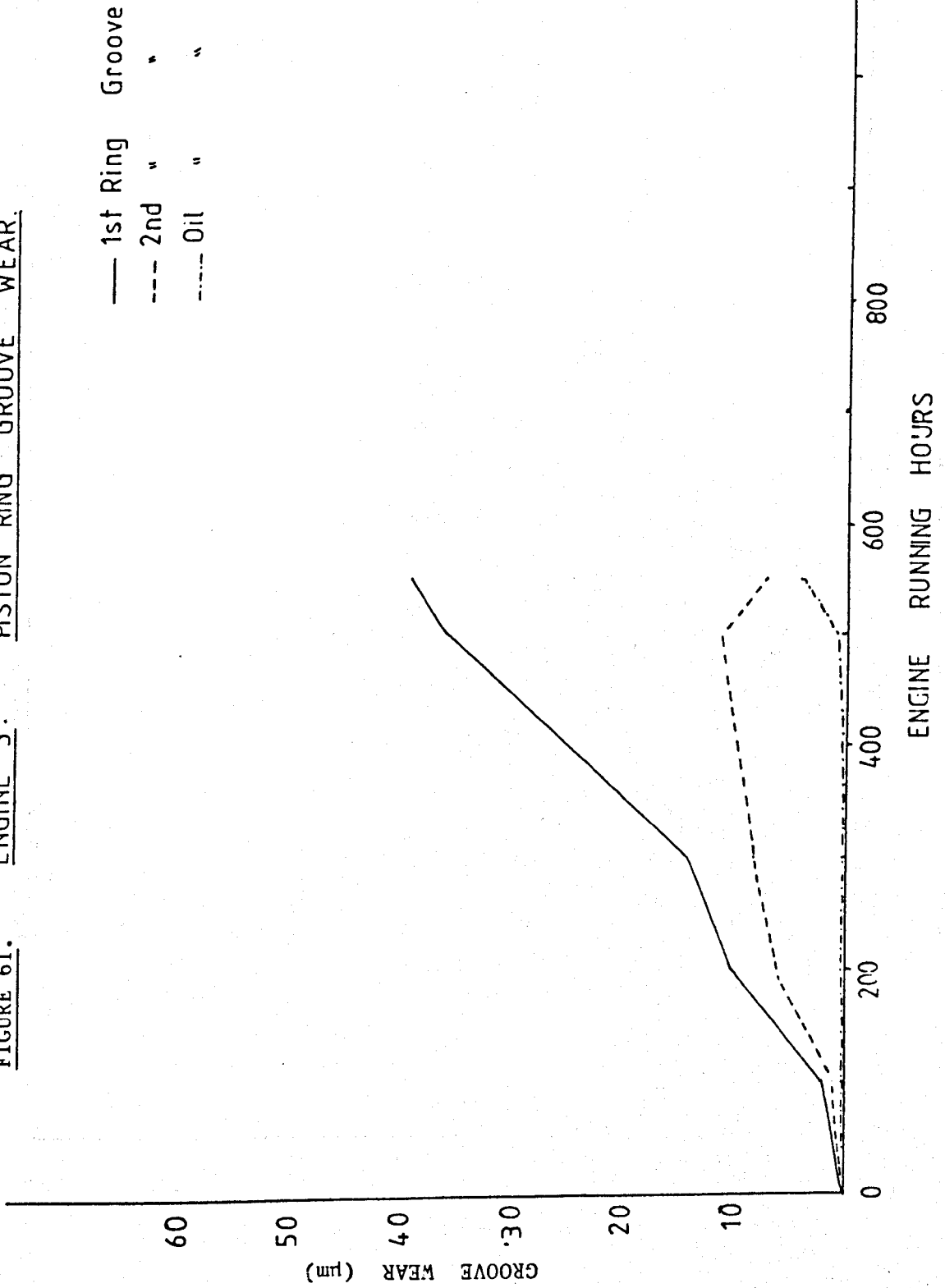
▲ 1st Comp. Ring  
 × 2nd Comp. Ring



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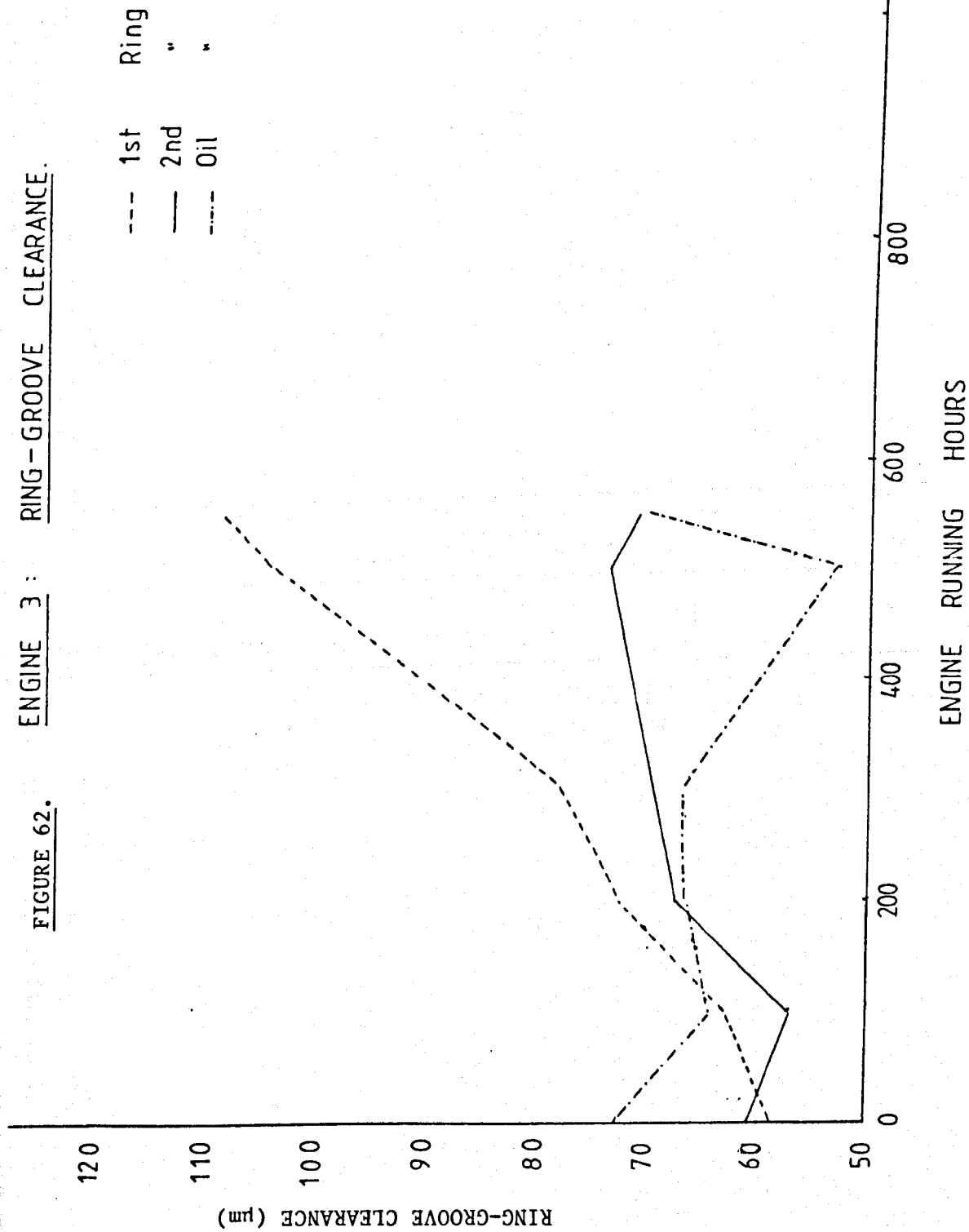
FIGURE 61.      ENGINE 3:      PISTON RING GROOVE WEAR.



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NAME

ENGINE 3 : RING - GROOVE CLEARANCE.



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NAME



FIGURE 63. ENGINE 2 OIL CONSUMPTION AS A % OF FUEL FLOW

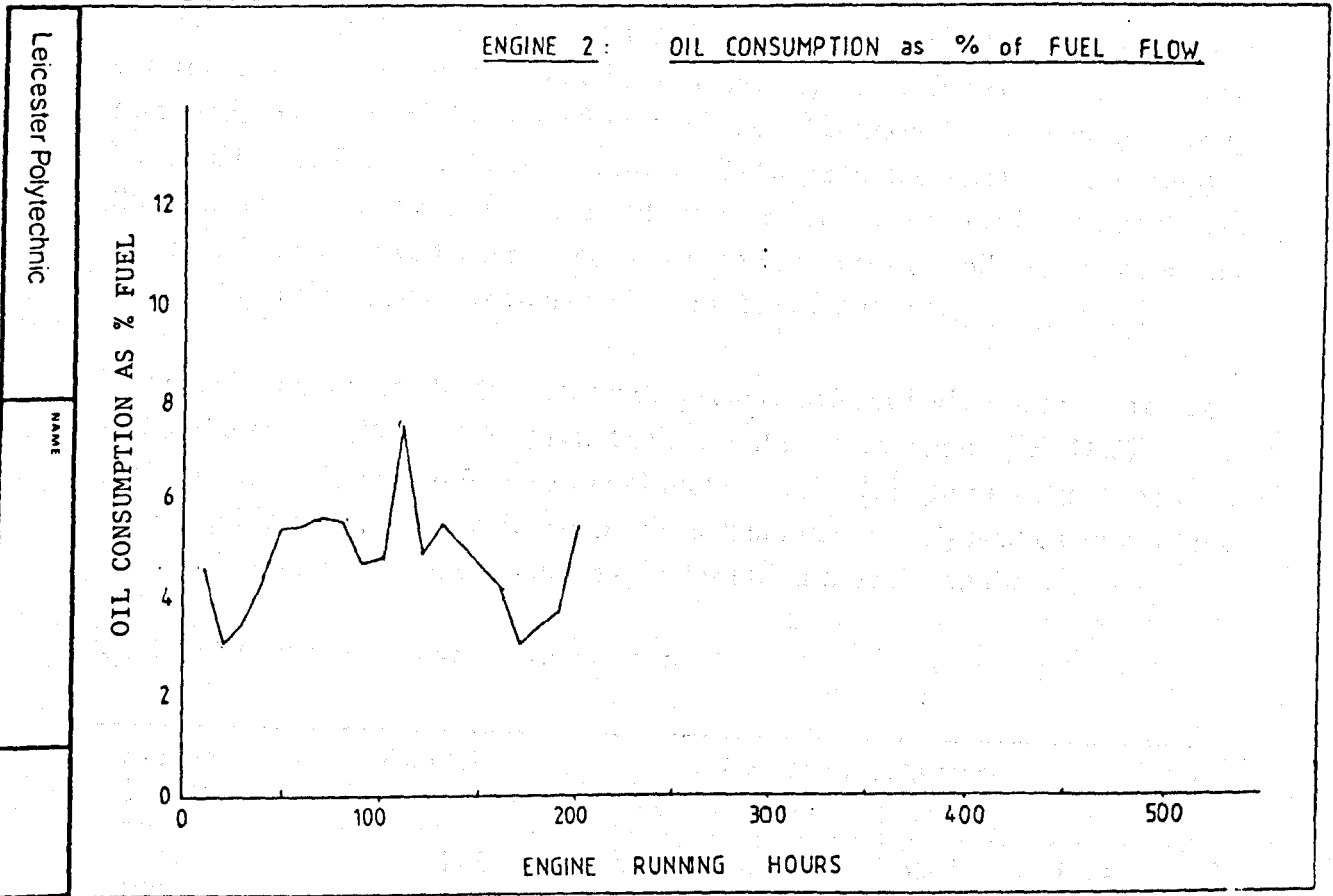
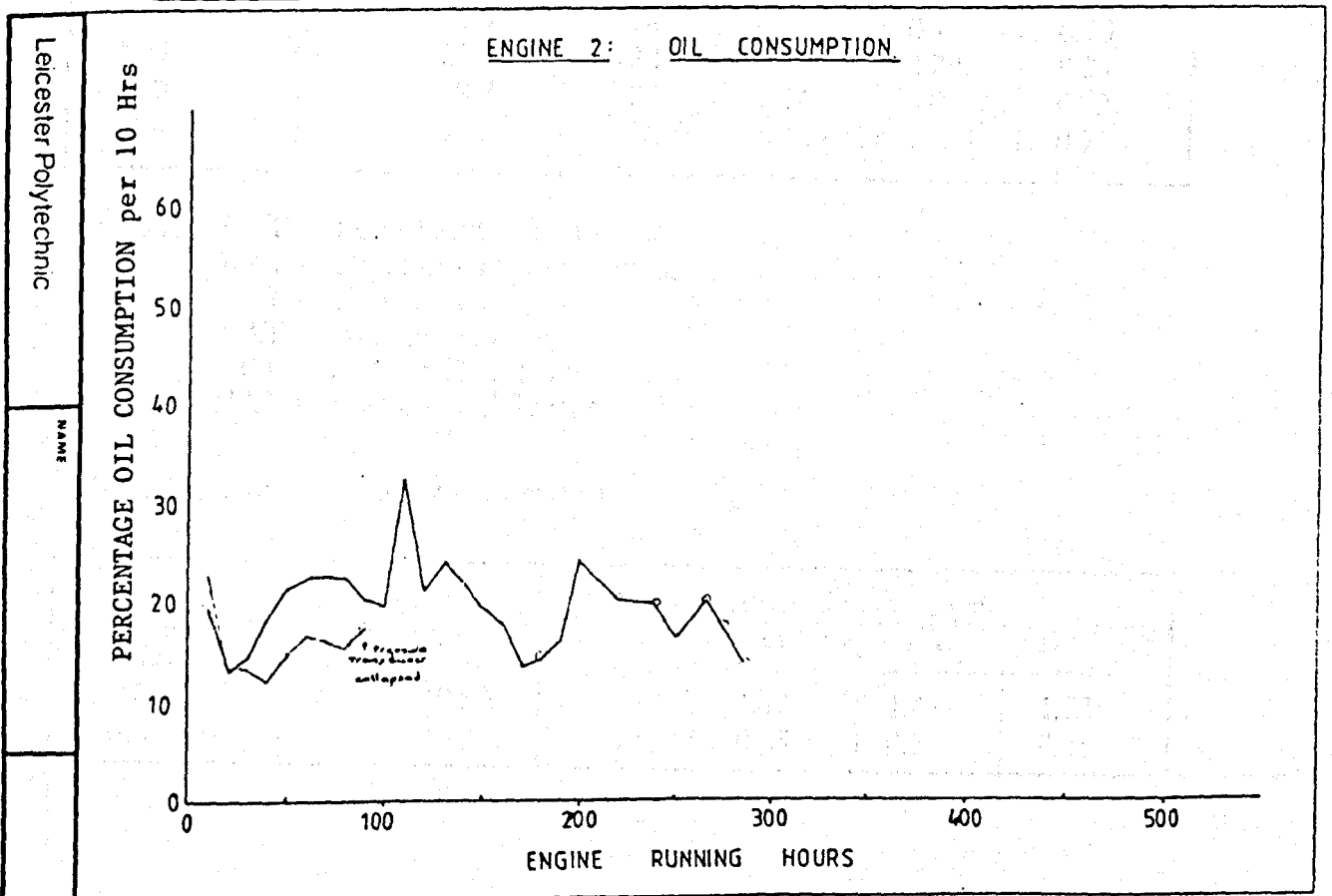


FIGURE 64. ENGINE 2 OIL CONSUMPTION.



The engine that received regular servicing, engine E2, although showing a higher level of oil consumption than the other engine (E3), also showed a loss of oil consumption control at about the same total number of engine operating hours, see Table 33 and Figures 63, 64. Engine E2 was run for three hundred hours with an oil change at every hundred hours. Engine E3 was run with no oil change for the duration (550 hours) of the test. The engines were stripped and measured after every one hundred hours of running. It was observed that the engines showed an increase in oil consumption after reassembly which then decreased to a lower value as the running progressed.

The conclusion that can be drawn from the premature loss of oil consumption control is that the engine (Petter AA-1) is not suited to the lubricating oil (OMD-75) or the high sulphur (1% m/v) reference diesel fuel or both. It is probable that the bore polishing is a result of corrosive wear arising from the strongly acidic nature of the combustion products of the gas in the cylinder rather than that in the oil.

**TABLE 32.** ENGINE 3 WEAR AND OIL CONSUMPTION.

Engine Hours	(% ) Oil Consumption	Centre Line Average			
		LAT	RAT	T	AT
0	17.0	0.91	1.28	0.65	0.54
100	13.0	0.63	0.31	0.31	0.71
200	6.0	0.53	0.34	0.32	0.34
300	8.7	0.31	0.29	0.14	0.24
400	9.9	0.24	0.30	0.17	0.20
500	29.5	0.30	0.23	0.20	0.24
550	38.7	0.28	0.22	0.07	0.32
550	38.7	Unworn part of bore			0.71

**NOTE:** LAT = Left of Anti-thrust Axis,  
 RAT = Right of Anti-thrust Axis,  
 T = Thrust Axis,  
 AT = Anti-thrust Axis,  
 BT = Bottom Thrust side, and  
 BAT = Bottom Anti-Thrust side.

**TABLE 33.** ENGINE 2 WEAR AND OIL CONSUMPTION.

Engine Hours	(% ) Oil Consumption	Centre Line Average			
		T	AT	BT	BAT
0	19.50	1.60	1.12	1.47	1.72
100	19.8	0.39	0.35	0.79	0.85

The unexpected, premature and extensive nature of the bore polishing rendered the further testing of the oil degradation investigation useless. The high rate of replenishment of the used oil in the sump with fresh oil (make-up) would mask any noticeable oil degradation from being observed. It is for this reason that further oil testing was stopped in favour of furthering the oil analysis techniques for the determination of TAN, TBN, water content and Total Insoluble Matter, and the automation of these analyses.

#### 4.8.2 Engine Oil Analyses.

The oil analysis results for each of the engine test runs 2A, 2B, 2C, 3A, 3B, 3C and 3DEF are summarised in the tables 34 to 40, respectively. The trends of each of the oil parameters is discussed briefly below.

**TBN.** The TBN (IP 276) values diminish to a stabilised value of about 4.5 mg KOH/g and are consistent for all test runs. The period by which time stabilisation of the TBN value occurs is approximately 30 to 40 hours of testing.

**TAN.** The TAN values on the other hand, generally rise rapidly to a value of 1.9 mg KOH/g and thereafter tend to rise at a reduced rate.

**Viscosity.** The viscosity at 20 °C and 40 °C generally increase with time whereas the 100 °C value decreases with time. The level of oil consumption, and therefore, the amount of top-up, moderates the changes in level of the viscosity.

**Zinc and Phosphorus.** The difference in amount of zinc and phosphorus levels appeared to remain in constant proportion through all the test runs. The levels of these two elements increased linearly throughout the test runs.

**Iron.** The iron levels showed greater percentage change in levels than any of the other wear metals. Its general rising trend during a test run was moderated only by high oil consumption.

**Other Metals.** In almost all cases and for all test runs, the amounts of metals generally increased with time.

**Oil Blackness.** The intensity of the blackness quality of the used oil increased with time and was moderated only by high levels of oil consumption.

TABLE 34. OIL ANALYSIS RESULTS FOR THE FIRST 100 HOUR TEST (2A) ON ENGINE 2.

TEST SERIES: 2A OIL HOURS: 0 - 100 ENGINE HOURS: 0 - 100

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.085	0.080	9	2	1	3	2	5	4	0.00	0.0	0	1500	0.000	
10	5.71	2.01	34.0	17.4	3.80	0.20	0.085	0.080	22	4	1	3	2	8	4	2.37	23.0	0	1538	0.000	-0.0417
20	4.45	2.10	47.2	20.0	4.30	0.21	0.085	0.080	23	4	1	4	3	10	4	4.30	13.7	400	1553	2.240	0.1240
30	4.64	3.60	38.6	23.8	5.10	0.22	0.085	0.080	27	5	1	4	3	10	4	5.74	13.6	236	1602	1.322	0.2456
40	4.02	4.83	31.9	18.0	4.80	0.23	0.090	0.080	30	5	2	4	4	11	4	7.68	12.4	235	1600	1.316	0.3290
50	4.13	5.11	47.6	18.7	3.40	0.23	0.090	0.080	34	5	2	4	3	11	4	10.26	15.0	217	1621	1.215	0.4792
60	4.77	4.83	48.9	18.8	3.80	0.24	0.090	0.085	36	5	2	5	3	13	4	12.67	16.8	258	1601	1.445	0.4387
70	4.15	4.98	47.9	18.0	3.00	0.25	0.090	0.085	38	5	2	5	4	12	4	15.10	16.2	288	1600	1.613	0.6532
80	3.22	4.25	53.0	19.9	4.00	0.26	0.095	0.090	40	5	2	5	4	12	4	19.80	15.5	270	1613	1.512	0.6723
90	3.97	5.34	51.8	21.2	3.50	0.26	0.095	0.090	43	6	3	6	4	12	5	24.10	17.3	270	1511	1.630	0.8154
100	4.60	5.60	53.0	22.4	3.90	0.26	0.095	0.090	40	6	3	6	4	12	5	28.30	18.2	291	1601	1.750	0.6175

**TABLE 35. OIL ANALYSIS RESULTS FOR THE SECOND 100 HOUR TEST (2B) ON ENGINE 2.**

**TEST SERIES: 2B**

**OIL HOURS: 0 - 100**

**ENGINE HOURS: 0 - 100**

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.080	0.075	22	2	1	3	2	5	4	0.00	0.0	0	1500	0.000	
10	5.00	1.68	41.2	19.5	4.10	0.20	0.085	0.080	32	4	1	5	2	6	4	3.33	19.8	0	1497	0.000	-0.4411
20	4.86	1.82	42.6	20.6	4.40	0.21	0.085	0.080	29	4	1	4	2	7	5	4.54	13.1	334	1497	1.870	0.1120
30	4.51	1.72	47.7	21.2	4.40	0.22	0.090	0.080	30	4	1	4	2	7	4	5.73	14.4	269	1504	1.506	0.4315
40	4.74	2.05	47.4	20.0	4.00	0.23	0.090	0.085	35	4	1	4	2	7	4	8.00	18.3	145	1497	0.812	0.6437
50	4.89	1.85	48.0	20.7	4.40	0.24	0.090	0.085	36	4	2	4	2	8	4	9.81	21.5	328	1498	1.837	0.9489
60	4.87	2.04	49.6	21.2	4.50	0.25	0.090	0.085	35	4	2	5	2	8	4	10.78	22.7	334	1502	1.870	1.1873
70	4.85	2.02	50.0	21.4	4.20	0.26	0.095	0.085	35	4	2	5	2	8	5	10.67	22.6	376	1495	2.106	1.3542
80	4.80	2.13	50.0	20.7	4.10	0.27	0.095	0.085	34	4	2	5	2	9	5	11.94	22.5	389	1506	2.178	1.4603
90	5.31	2.08	52.5	21.2	4.00	0.28	0.100	0.090	35	4	3	6	3	8	5	14.10	20.3	280	1503	1.568	1.7189
100	4.95	2.05	50.6	20.8	4.00	0.25	0.090	0.080	29	4	2	5	3	9	4	16.26	19.9	416	1502	2.330	1.7833

**TABLE 36. OIL ANALYSIS RESULTS FOR THE THIRD 100 HOUR TEST (2C) ON ENGINE 2.**

**TEST SERIES: 2C**

**OIL HOURS: 0 - 100**

**ENGINE HOURS: 0 - 100**

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.080	0.075	22	2	1	3	2	5	4	0.00	0.0	0	1500	0.000	
10	6.23	1.68	47.8	17.8	2.80	0.21	0.085	0.075	13	2	1	3	6	5	4	3.81	32.4	0	1497	0.000	0.1335
20	5.29	1.82	49.4	18.7	2.80	0.22	0.085	0.080	9	2	1	3	5	6	4	7.13	21.2	498	1497	2.789	0.3338
30	5.62	1.72	49.8	19.8	2.70	0.23	0.090	0.080	12	2	2	4	5	5	4	9.42	23.9	336	1504	1.882	0.5770
40	5.29	2.05	51.8	19.2	2.80	0.24	0.090	0.080	16	2	2	4	5	6	4	12.05	22.0	365	1497	2.044	0.6127
50	5.83	1.85	53.4	20.1	2.80	0.25	0.095	0.080	19	3	2	5	6	6	5	15.01	19.6	348	1498	1.949	0.6771
60	5.42	2.04	54.4	20.4	2.40	0.25	0.095	0.085	20	3	2	5	6	6	4	19.87	18.1	314	1502	1.758	0.8380
70	5.01	2.02	54.4	20.4	2.40	0.26	0.095	0.085	22	3	3	6	6	6	4	19.87	13.6	272	1495	1.523	0.9989
80	5.51	2.13	55.1	19.9	3.10	0.27	0.100	0.085	24	3	3	6	5	7	5	22.47	14.7	229	1506	1.282	1.1134
90	5.35	2.08	56.4	20.4	3.00	0.27	0.100	0.090	26	3	3	7	6	7	5	25.80	16.0	236	1503	1.322	1.2213
100	5.16	2.05	58.4	20.7	3.00	0.28	0.100	0.090	28	3	3	7	6	7	5	29.30	24.0	245	1502	1.372	1.3291

TABLE 37. OIL ANALYSIS RESULTS FOR THE FIRST 100 HOUR TEST (3A) ON ENGINE 3.

TEST SERIES: 3A OIL HOURS: 0 - 100 ENGINE HOURS: 0 - 100

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.080	0.075	22	2	1	3	2	5	4	0.00	0.0	0	1500	0.000	
10	5.10	2.42	48.0	19.2	4.20	0.22	0.080	0.080	19	2	2	4	18	11	19	23.80	15.2	0	1444	0.000	0.8690
20	4.47	1.70	49.8	19.2	3.70	0.23	0.090	0.085	46	8	4	6	6	12	8	32.90	13.9	0	1298	0.000	0.5579
30	4.30	1.68	53.9	19.9	3.50	0.24	0.095	0.085	51	8	4	7	5	12	6	39.90	19.5	0	1136	0.000	0.6199
40	4.30	1.76	67.8	24.0	3.70	0.21	0.100	0.090	47	8	4	7	6	12	6	37.10	14.5	398	1290	2.229	-1.4793
50	4.23	1.38	66.6	24.1	4.00	0.22	0.100	0.090	53	11	5	8	7	12	7	39.40	14.8	244	1315	1.366	-0.8940
60	4.45	1.94	59.8	23.1	5.90	0.24	0.100	0.090	56	15	6	10	7	13	7	29.90	15.9	277	1375	1.551	-0.3004
70	3.16	1.61	62.9	23.1	4.00	0.26	0.105	0.090	60	19	6	10	7	13	7	40.10	17.7	268	1403	1.501	-0.0164
80	3.74	1.33	55.4	23.3	6.50	0.26	0.105	0.095	66	25	6	12	7	14	7	39.60	28.7	202	1333	1.131	0.3624
90	4.56	1.58	64.4	25.2	4.60	0.27	0.105	0.095	65	102	5	10	19	14	16	54.90	24.5	364	1292	2.038	0.8797
100	4.36	1.85	61.3	22.4	3.70	0.27	0.105	0.095	65	143	6	12	13	15	14	41.70	22.6	459	1413	2.570	1.5187

**TABLE 38. OIL ANALYSIS RESULTS FOR THE SECOND 100 HOUR TEST (3B) ON ENGINE 3.**

**TEST SERIES: 3B OIL HOURS: 0 - 100 ENGINE HOURS: 100 - 200**

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.080	0.075	22	2	1	3	2	5	4	0.00	0.0	0	1500	0.000	
10	4.47	2.56	46.2	17.6	2.90	0.20	0.080	0.080	23	8	1	5	1	4	4	5.20	17.0	0	1423	0.000	-0.0811
20	4.44	2.59	46.9	17.8	3.10	0.20	0.090	0.080	24	10	1	5	2	5	4	6.00	14.5	4.08	1585	2.285	0.0167
30	4.29	2.62	48.9	18.4	3.10	0.21	0.090	0.080	19	10	1	4	1	6	4	8.21	17.3	1.65	1499	0.924	0.3648
40	4.22	2.52	48.3	18.8	3.10	0.22	0.090	0.080	32	17	2	7	1	8	4	10.80	16.1	2.04	1422	1.142	0.4899
50	4.22	2.61	49.6	18.7	3.30	0.26	0.100	0.090	40	24	4	8	3	3	4	11.80	15.1	1.84	1358	1.030	0.8702
60	4.08	2.36	51.7	20.3	3.60	0.24	0.090	0.080	33	18	2	6	1	5	4	12.80	13.9	1.80	1429	1.008	0.7987
70	4.02	2.31	51.5	19.1	3.30	0.23	0.090	0.080	35	18	2	7	1	6	4	14.40	14.8	2.83	1490	1.585	0.6675
80	4.19	1.93	51.6	19.6	3.30	0.24	0.090	0.080	40	22	3	8	1	6	4	16.30	15.3	1.54	1402	0.862	0.9799
90	4.02	2.49	52.0	19.4	3.60	0.25	0.100	0.090	32	17	3	7	5	7	5	15.10	12.9	4.09	1569	2.290	0.9036
100	4.30	2.41	51.6	19.2	3.60	0.25	0.100	0.090	33	17	3	6	4	7	5	15.80	13.1	2.52	1590	1.411	0.8523



**TABLE 39. OIL ANALYSIS RESULTS FOR THE THIRD 100 HOUR TEST (3C) ON ENGINE 3.**

**TEST SERIES: 3C**

**OIL HOURS: 100 - 200**

**ENGINE HOURS: 200 - 300**

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
100	4.30	2.41	51.6	19.2	3.60	0.25	0.100	0.090	33	17	3	6	4	7	5	15.80	13.1	252	1590	1.411	0.8523
110	4.89	1.60	46.7	17.6	3.40	0.20	0.080	0.080	22	9	2	6	4	6	4	3.50	12.1	0	1592	0.000	-0.1621
120	4.85	1.60	47.8	22.9	3.30	0.20	0.090	0.080	12	7	1	6	2	6	3	5.60	11.6	219	1599	1.226	0.1025
130	4.72	1.61	48.9	19.0	3.40	0.21	0.090	0.080	29	11	2	6	2	7	3	9.00	12.1	206	1602	1.154	0.3147
140	4.41	1.61	50.8	19.0	3.10	0.22	0.090	0.080	18	9	1	3	2	7	3	11.00	8.5	222	1612	1.243	0.4005
150	4.84	1.61	52.6	20.0	3.60	0.22	0.090	0.080	29	12	3	7	3	8	3	12.90	8.1	149	1603	0.834	0.6485
160	5.12	1.61	54.4	21.8	3.60	0.23	0.090	0.080	31	13	3	6	1	8	3	14.10	7.9	146	1601	0.818	0.8273
170	5.00	1.87	54.4	21.8	3.60	0.24	0.100	0.090	44	17	5	9	2	10	3	16.40	7.4	146	1600	0.818	0.6127
180	4.85	1.87	51.4	20.8	3.60	0.25	0.100	0.090	40	16	4	8	1	7	5	18.70	6.6	108	1581	0.605	1.0323
190	4.38	1.57	53.5	21.4	4.20	0.25	0.100	0.090	37	15	4	8	1	7	5	19.70	5.4	146	1602	0.818	1.0556
200	4.99	1.37	54.4	23.2	4.70	0.26	0.100	0.090	43	17	5	9	2	8	5	22.10	5.9	106	1603	0.594	1.0788

**TABLE 40. OIL ANALYSIS RESULTS FOR THE 300 HOUR TEST (3F) ON ENGINE 3.**

**TEST SERIES: 3F OIL HOURS: 0 - 300 ENGINE HOURS: 300 - 600**

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.080	0.075	22	2	1	3	2	5	4	0.00	0.0	0	1500	0.000	
34	5.12	1.91	43.3	17.6	3.60	0.21	0.080	0.080	29	9	3	6	2	4	5	9.10	6.7	0	1350	0.000	0.0358
66	4.62	1.90	50.8	20.8	4.00	0.26	0.100	0.090	33	12	3	9	1	5	5	12.90	6.7	470	1350	2.632	1.3685
84	4.68	2.14	51.1	20.4	4.00	0.26	0.100	0.090	32	11	3	8	1	4	5	11.60	6.7	884	1546	4.950	1.5664
100	4.61	1.92	52.6	21.1	4.00	0.26	0.100	0.090	25	9	3	8	1	5	5	11.50	6.7	593	1540	3.321	1.4162
130	4.58	2.01	45.0	17.3	3.40	0.28	0.100	0.090	34	11	3	8	1	4	5	19.10	8.9	285	1331	1.574	1.8572
162	4.95	2.01	56.6	22.4	4.10	0.28	0.100	0.090	36	12	3	10	1	5	5	22.20	10.3	660	1331	3.696	2.0527
182	4.76	2.01	60.2	23.5	4.20	0.31	0.110	0.100	44	14	3	11	1	6	6	27.30	10.3	409	1331	2.290	2.6225
200	4.72	2.01	54.6	21.4	3.70	0.34	0.120	0.100	48	16	3	14	2	7	6	31.70	10.3	586	1331	3.282	3.1136
233	4.69	2.01	60.8	24.0	4.00	0.34	0.120	0.110	41	13	4	13	5	12	6	25.50	8.7	725	1331	4.060	2.9158
262	4.76	2.01	56.0	20.5	3.80	0.30	0.110	0.100	26	7	3	9	5	8	6	15.60	23.7	700	1221	4.883	1.8691
270	5.49	2.01	55.4	21.2	3.10	0.31	0.120	0.100	27	8	3	9	3	9	6	18.00	34.0	391	1602	2.190	2.0789
280	5.27	2.01	55.8	23.4	2.90	0.31	0.120	0.100	33	8	3	10	3	9	6	16.10	42.9	561	1604	3.124	1.8572
290	5.89	2.01	52.6	19.4	2.90	0.29	0.110	0.100	22	6	2	7	3	8	6	12.90	23.9	703	1606	3.937	1.6713
300	5.05	2.01	57.6	21.6	3.10	0.30	0.110	0.100	23	6	2	7	2	7	6	12.30	40.8	390	1600	2.184	2.0503

**Total Insoluble Matter.** The initial trend for TIM was a rapid increase in the first 30 hours of the test, after which its level stabilised or changed to a slower rate of increase. The TIM level, like most of the other parameters mentioned above, was also moderated by the amount of oil make-up.

**Oxidation.** The amount of oxidation products generally increased in proportion to the amount of oil blackness, with the age of the oil. The level of oxidants decreased on addition of large quantities of fresh oil (make-up).

#### 4.9 OIL TREND ANALYSIS.

The brief trend analysis given above was deduced from the tables of data. An in-depth correlation and trend analysis can be obtained from a graphical representation of the results. The raw data were smoothed (mathematically) and (quadratic) curve-fitted when plotted in the graphs that follow, below, to clearly show any trends and to allow average rates of change of the parameters to be elucidated. From the discussion given in the previous section, the parameters can be grouped into various categories. Two categories that are evident from the data are:

- (a) parameters that increase in concentration with the age of the oil, and
- (b) those parameters whose concentration decrease with the age of the oil.

Only two parameters fall into the latter category, namely, TBN and 100 °C Viscosity. All the rest of the parameters fall into the former category, where their respective concentrations increase with the age of the oil.

The large number of oil parameters that show an increase in concentration with the aging of the oil, can be further sub-divided into:

1. those parameters that appear to behave similarly and have some proportional relationship to each other, and
2. those parameters that do not have a proportional relationship to those mentioned in (1) above, but may or may not be related proportionally to other parameters.

Each of these categories will now be examined and discussed in relation to the relevant parameters.

#### 4.9.1 TBN.

The TBN values are expected to decrease with the aging of the oil. The rate of TBN depletion will depend on the amount of acids entering the oil that become neutralised, the amount of fresh TBN added from oil make-up, and also on the initial TBN concentration (of the new oil). The first and second parts of the above statement requires no explanation. The dependence of the TBN value of the used oil on the initial (new oil) TBN value, requires some explanation.

The TBN value of a new oil when determined by IP 177 measures the inorganic (strong) TBN, whereas that determined by IP 276, measures both the inorganic and the (weaker) organic TBN as well. Therefore, the TBN determined by IP 276 does not represent a true measure of the oil's alkaline reserve. TBN as determined by IP 276, does in reality, over-estimate the alkaline reserve, for the reasons mentioned in Chapter 2, Section (2.1). The weak bases present in the new and used oil probably are ineffective in neutralising the weaker (organic) acids. In any case, the more reactive alkaline additives present in the oil will become consumed in a very short space of time, from a theoretical treatise based on the percentage sulphur in fuel, blowby flow rate and composition of blowby gases (see Dyson model [33] and equation (39), page 200, Chapter 5). The period for the complete neutralisation of the inorganic TBN (be it be a gross over-estimate by IP 276 or not) can be shown to be in the region of a few hours. The "TBN" that remains within the used oil after three hours should approach zero, but this is seldom, if at all, observed in formulated oils. This is because:

1. most of the acids enter the exhaust,
2. most of the (acidic) blowby gases (e.g. sulphur dioxide) are dissolved in the oil without reacting with the TBN, and
3. the lack of water at elevated temperatures to convert the gases into acids.

The "TBN" that remains in the used oil, therefore, contains little, if any, effective (inorganic) neutralising reagents. The level of the non-effective (slow reacting), organic bases can, therefore, be expected to show relatively little change in TBN value as the organic bases can be burned during combustion along with the oil. This will hold true provided that the TAN value is not in excess over the TBN value. This has indeed been observed during the tests. Therefore, depending on the initial quantity of these weak bases present in the formulated oil, the TBN value of a oil after a few hours use will stabilise at some value lower than the original TBN value of the new oil.

Any TBN arising from fresh additions (oil top-ups) can be expected to become neutralised within a fraction of the time taken when beginning with a complete sump of fresh oil. This is because the used oil is now a reservoir consisting of a wide range of acids (amongst a myriad of other chemicals) and further additions of fresh acid during engine running will quickly seek out and neutralise the tiny amount of new, fast reacting, (inorganic) TBN reagent.

#### 4.9.2 100 °C Viscosity.

The kinematic viscosity of the used oil at 100 °C generally decreases initially during the first 30 hours of a test. The changes in viscosity although being small, does show a general increase, after 60 hours of testing. The reason for the initial decrease in viscosity at the high temperature, is due to shear thinning by removal of pendant groups from the (VII) polymers' carbon backbone and the breaking down of the long, polymer chain into smaller fragments of low molecular mass, thereby lowering the bulk viscosity. The viscosity increases again after the oil becomes oxidised by a significant extent, which then results in long chains of newly oxidised oil and polymer becoming cross-linked to give high molecular mass deposits and gums. The increase in soot content of the oil will also increase the viscosity of the oil.

#### 4.9.3 20 °C and 40 °C Viscosity.

The viscosity of the used oil at 20 °C and 40 °C appears to be closely related to one another. This may be the case as the two temperatures 20 °C (293 K) and 40 °C (313 K) are kinetically not very different from the standpoint of polymer and long hydrocarbon chain chemistry. The viscosity generally increases steadily throughout the aging of the oil, being moderated only by high oil make-up levels. The rise in viscosity is due to the longer, curled up, VII polymeric chains being fragmented to give a higher proportion of lower molecular weight polymers which increase the viscosity of the oil at low temperatures.

#### 4.9.4 Total Insoluble Matter and Oil Make-up.

The Total Insoluble Matter measurement appears to be closely related to the amount of oil make-up. The reason for this may be due to the dilution effect of adding new oil to a quantity which does not increase in level during the course of the test. This idea may not be as strange as it may seem for a quantity that is expected to rise continuously. Considering that the engine bedding-in period requires a fixed time to accomplish, the wear debris, oil stabilisation and engine stabilisation would then also be completed to a large extent. Therefore, no change in TIM can occur except through

a total loss mechanism and/or dilution, as has been observed.

#### 4.9.5 Oil Blackness, Oxidation, Iron and Calcium.

The blackness of the oil, the amount of oxidised material, the level of iron and calcium was found to increase linearly with the aging of the oil, similar to that of the oil viscosity at 20 °C and 40 °C. These components increase in level during the tests and appear not to be influenced, significantly, by oil make-up levels. Furthermore, these four components bear a proportional relationship between them and therefore, share a common mechanism.

It is interesting to note that these four components can be grouped together. The oil blackness and oxidation determinations are both measured by optical means and therefore share something in common. However, the blackness measurement is based on an absorbance measurement at a single (or narrow) wave band, whereas the oxidation measurement is derived from a complex mathematical treatment over a broader wave band. The blackness of the oil is a result of soot, gums, polymers, additives and wear debris interacting with infrared radiation. The oxidation level is a result of molecular interaction (excitation) present in the carbonyl group in an organic environment. The two optical measurements are, therefore, quite different in reality. The reason for the similarity in the results is their common mechanism.

The common mechanism that these four components share, together with all the wear metals and even the 20 °C and 40 °C viscosities, is two fold:

1. selective loss of combustible hydrocarbon only, that is, concentration by burning off the light fraction of the oil, and
2. selective aggregation and separation resulting in the prevention of components from being lost through a total loss mechanism, other than draining the oil from the sump.

The first mechanism involving selective loss of hydrocarbon can be visualised as taking place at the top-end of the engine only, at the combustion interface. Below this region, the engine oil can be considered as a more or less homogeneous mixture. The exception to this is the second mechanism. This relates not only to wear debris collecting in the bottom of the sump, but relates to all the engine internal surfaces, pipes, and any small pockets where deposits, gums, wear debris or surface coatings can accumulate or adhere.

Therefore, those components that give rise to the blackness of the oil, namely, soot,

finely dispersed wear debris, additives and oxidised (organic) compounds of high molecular mass, probably cannot be evaporated at the high temperatures in the engine top-end, so that they are forced into the combustion chamber where they can be burned. This, then, explains how some of the oil parameters increase with the ageing of the oil, almost unaffected by oil make-up levels in a constant volume situation.

The iron, wear metals and calcium present in the used oil may be dispersed not only by the polymeric dispersants, but also by the resins, gums and soot.

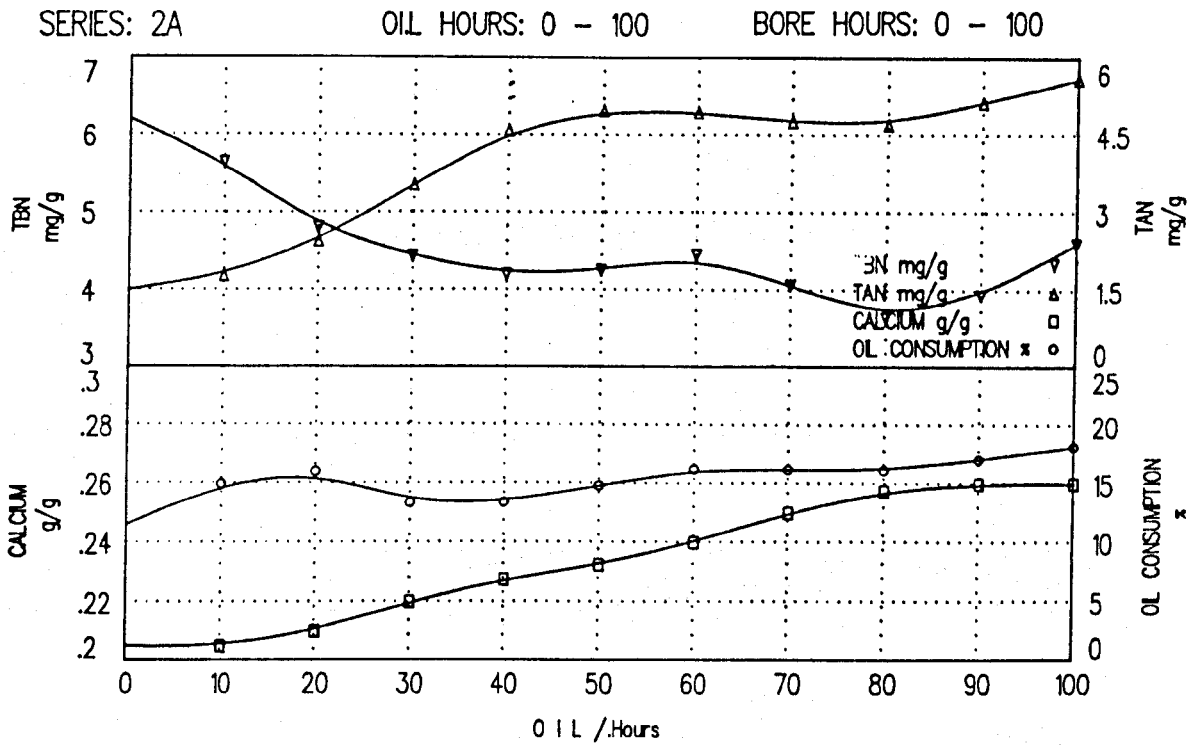
#### 4.9.6 Wear Metals, Sodium and Silicon.

The reason for the general increasing trend for the accumulation of wear metals has already been mentioned in the previous section above. The elements of most significance are iron, copper, chromium, and lead. The reason for this is that the levels of these elements relate information about the condition of the engine. Marked increases in the levels of these elements indicate that extra-ordinary engine wear is occurring, indicative of a failure or impending failure. This may arise due to the mechanical reasons or failures induced through chemical action of the oil. The steady rise in the levels of the elements monitored suggest normal wear has been taking place. The increasing levels of aluminium is from piston wear. The rise in the levels of silicon and sodium arise from the additive pack of the oil. The increase in the lead levels is due to lead being released from bearings as a result of wear and chemical leaching by acids present in the oil. A decrease in level of any of the wear elements would be indicative of total loss of oil, either through leaks or high oil consumption as a result of high wear.

#### 4.9.7 Zinc and Phosphorus.

These additive elements increase in level during the ageing of the oil. The rates of increase in the level of these two elements are in proportion to each other. However, when these rates are compared to the calcium level, another additive element, the calcium rate is found to be a factor of two to five times greater than that for the zinc or phosphorus. This would suggest that, whereas the calcium is showing accumulation, the zinc and phosphorus are not. The reason for the behaviour of zinc and phosphorus lies in their chemical behaviour. These elements are part of ZDDP, an anti-wear additive amongst its many properties. When the engine is worn, fresh layers of ZDDP would coat the newly exposed metal. Thus, zinc and phosphorus are removed from the oil by the wear debris. In addition, due to the suitability of ZDDP for forming ligands with oxidised components (organo-metallics), there is further possibility for

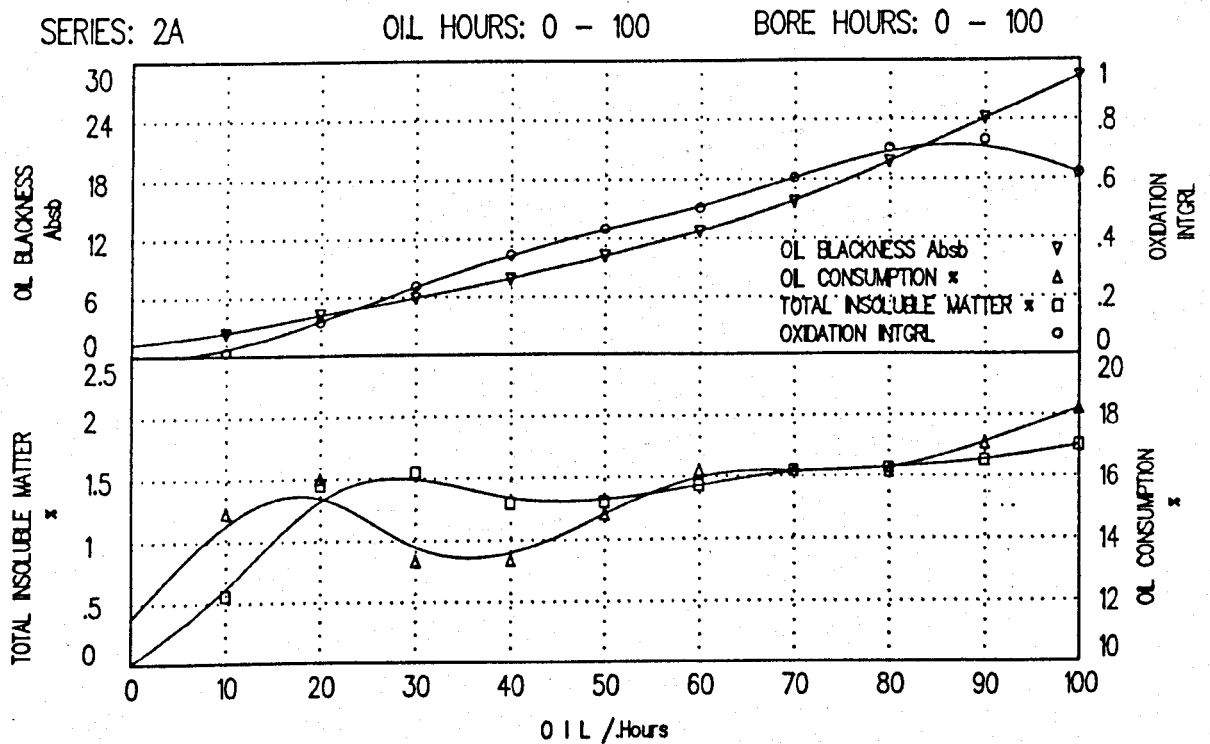
FIGURE 65 (a). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2A).



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FIGURE 66 (a). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2A).



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FIGURE 65 (b). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2B).

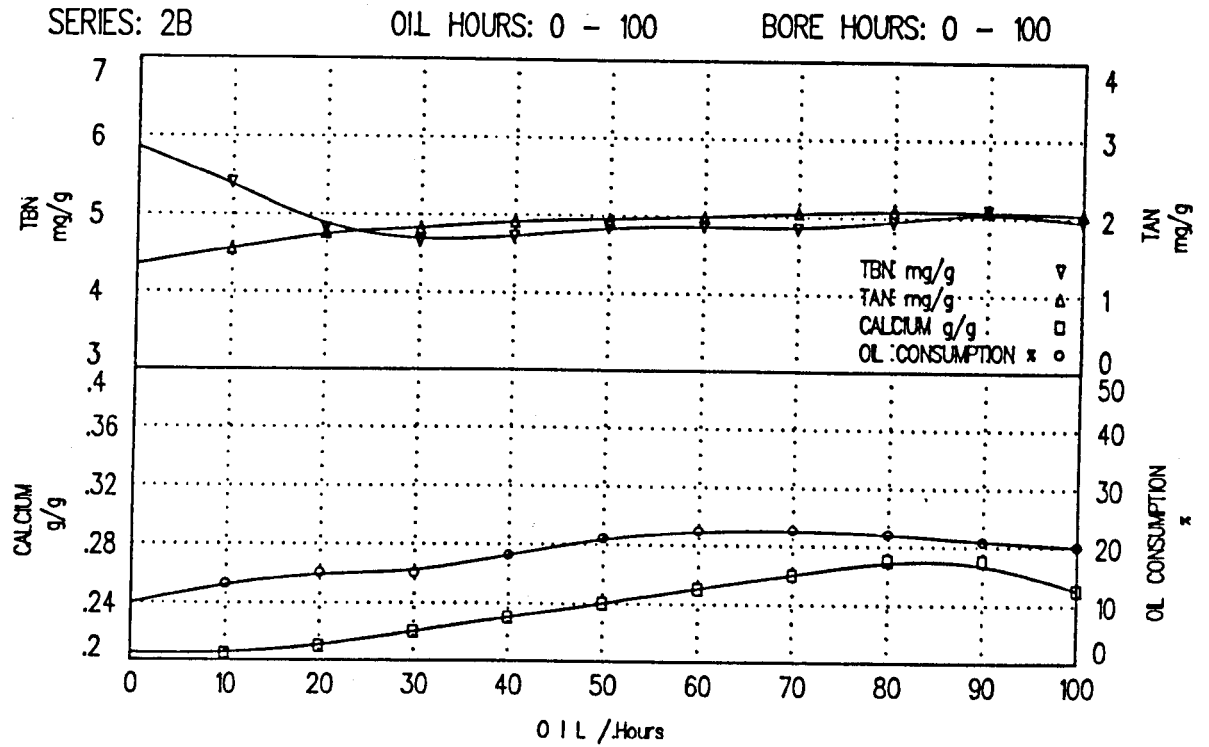


FIGURE 66 (b). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2B).

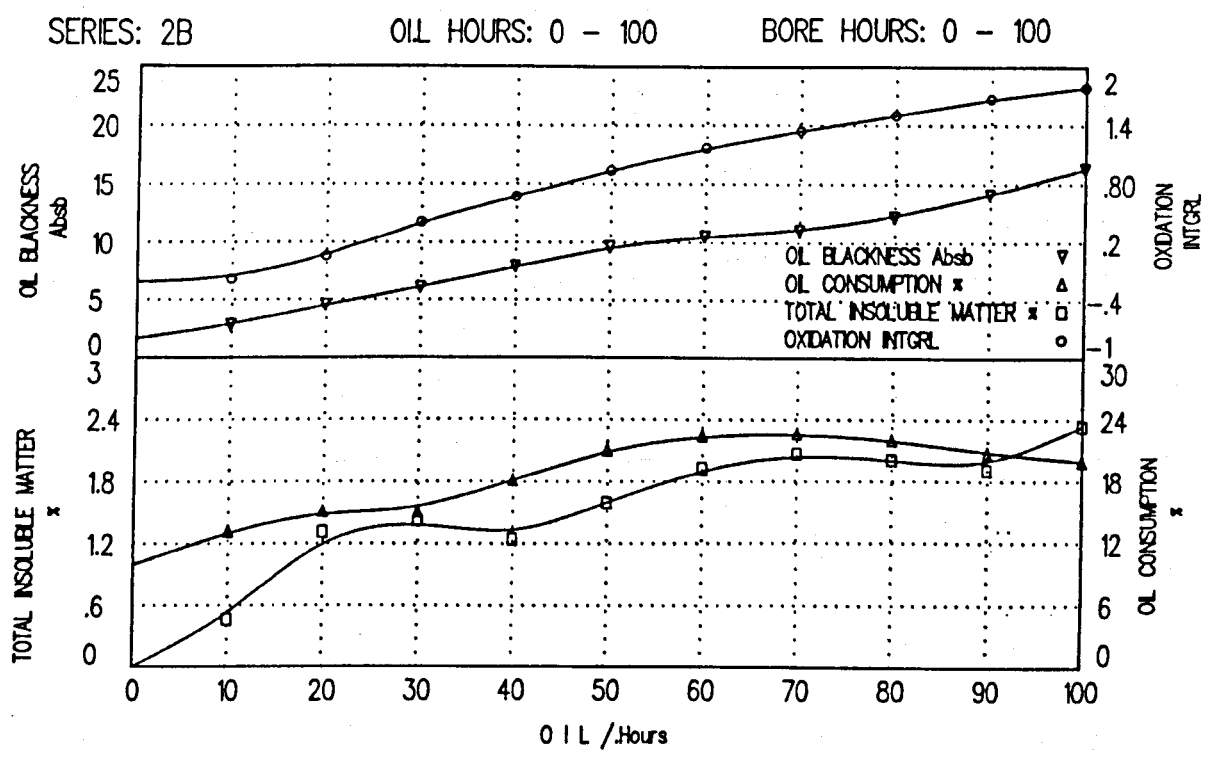
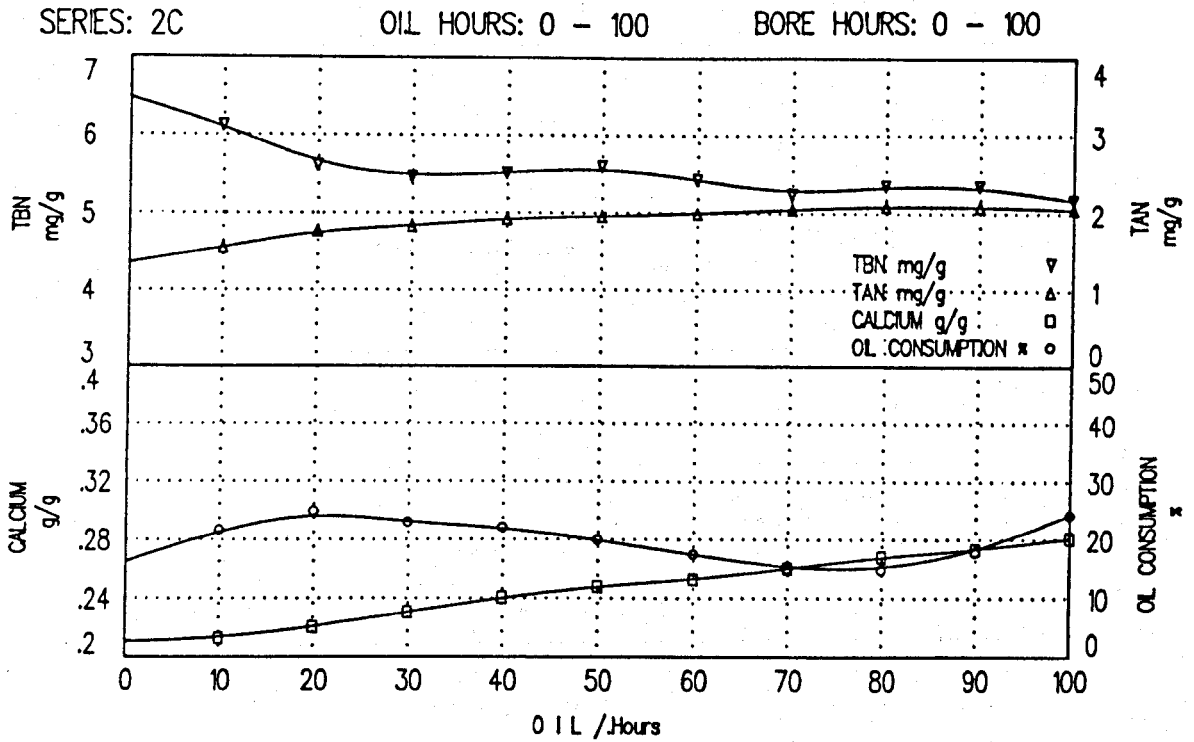


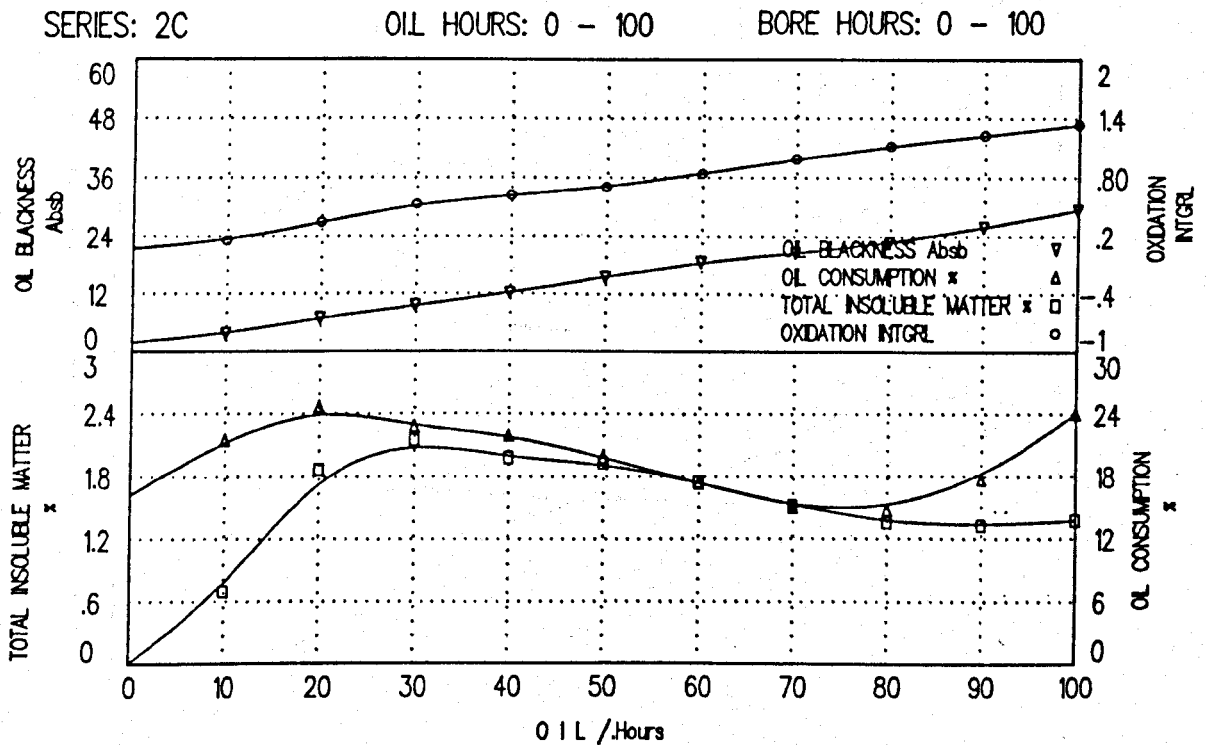
FIGURE 65 (c). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2C).



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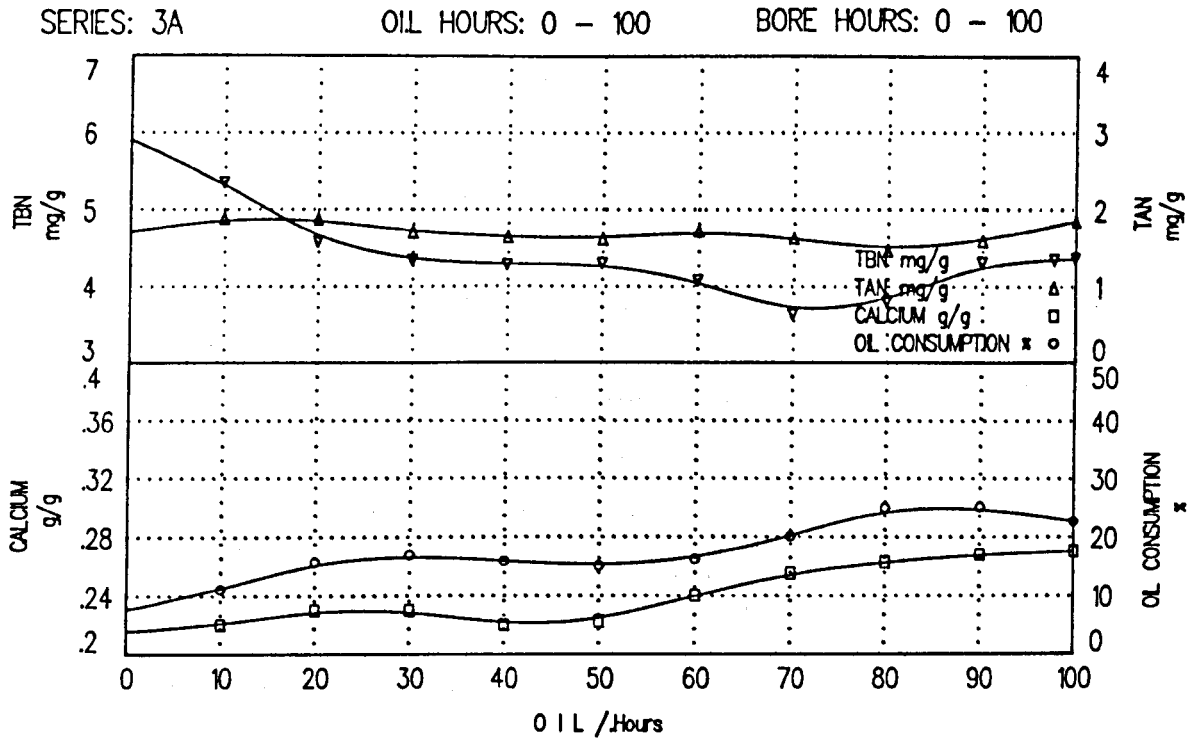
FIGURE 66 (c). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2C).



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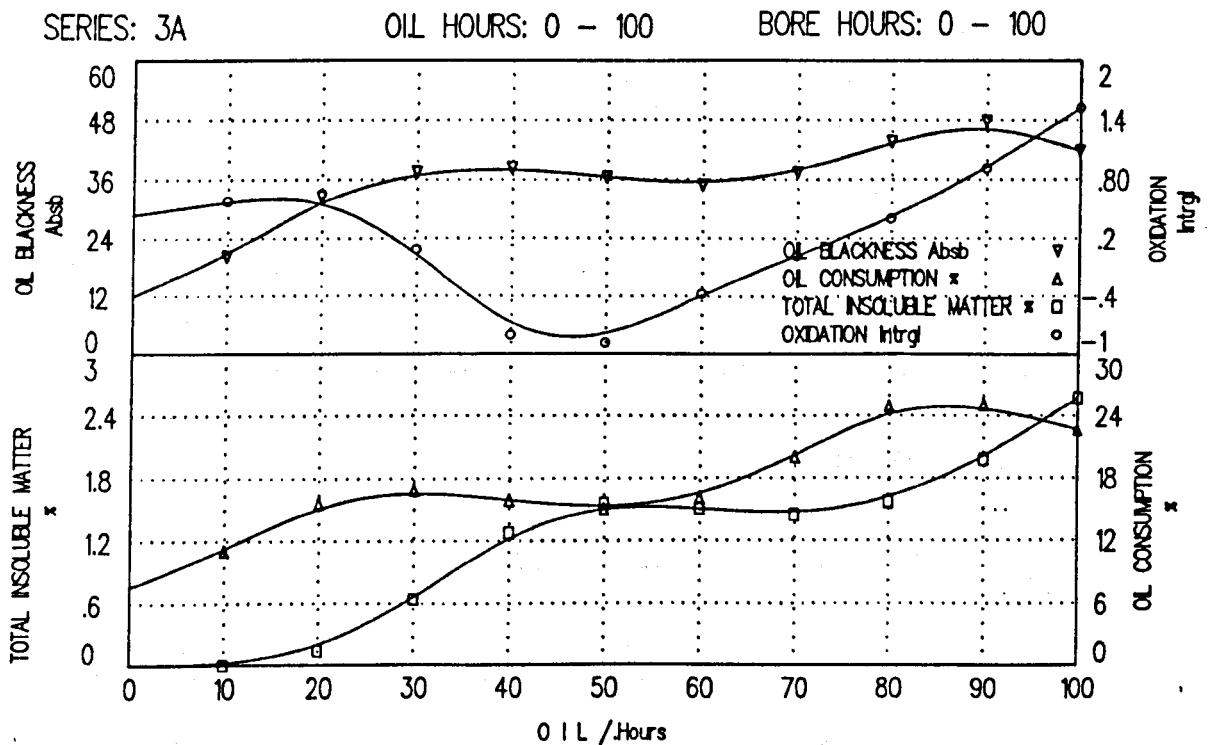
FIGURE 65 (d). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3A).



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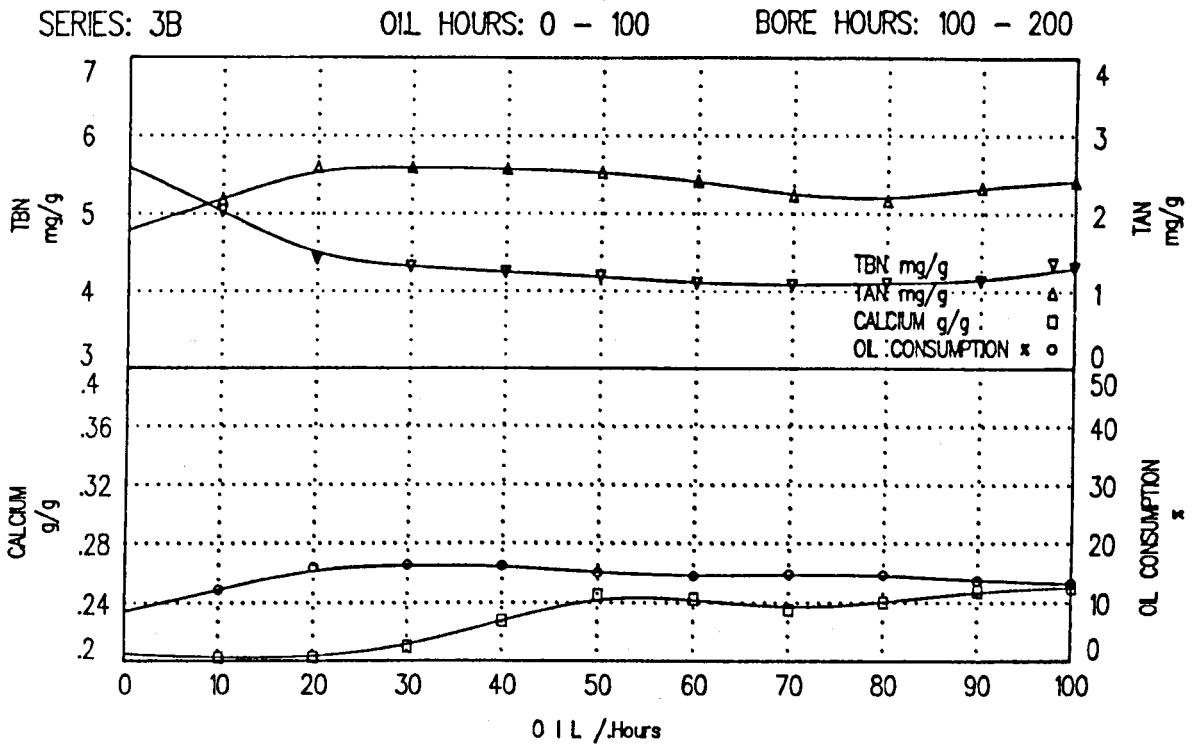
FIGURE 66 (d). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3A).



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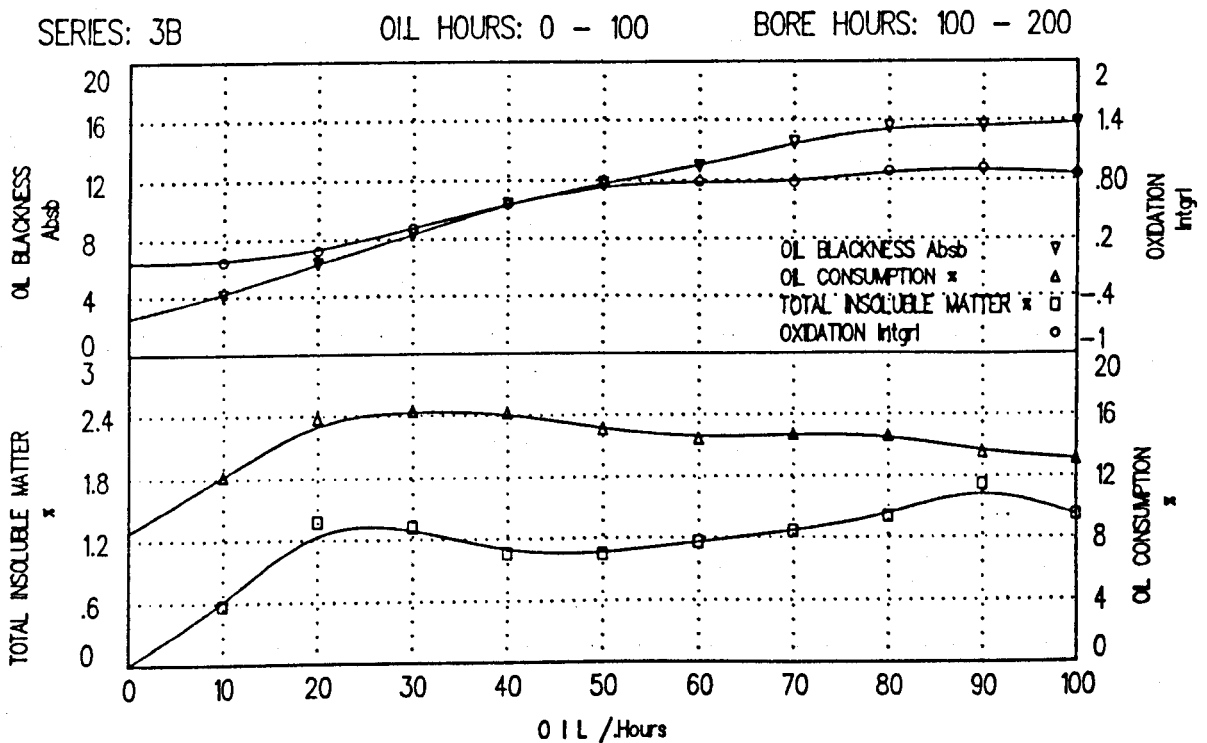
FIGURE 65 (e). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3B).



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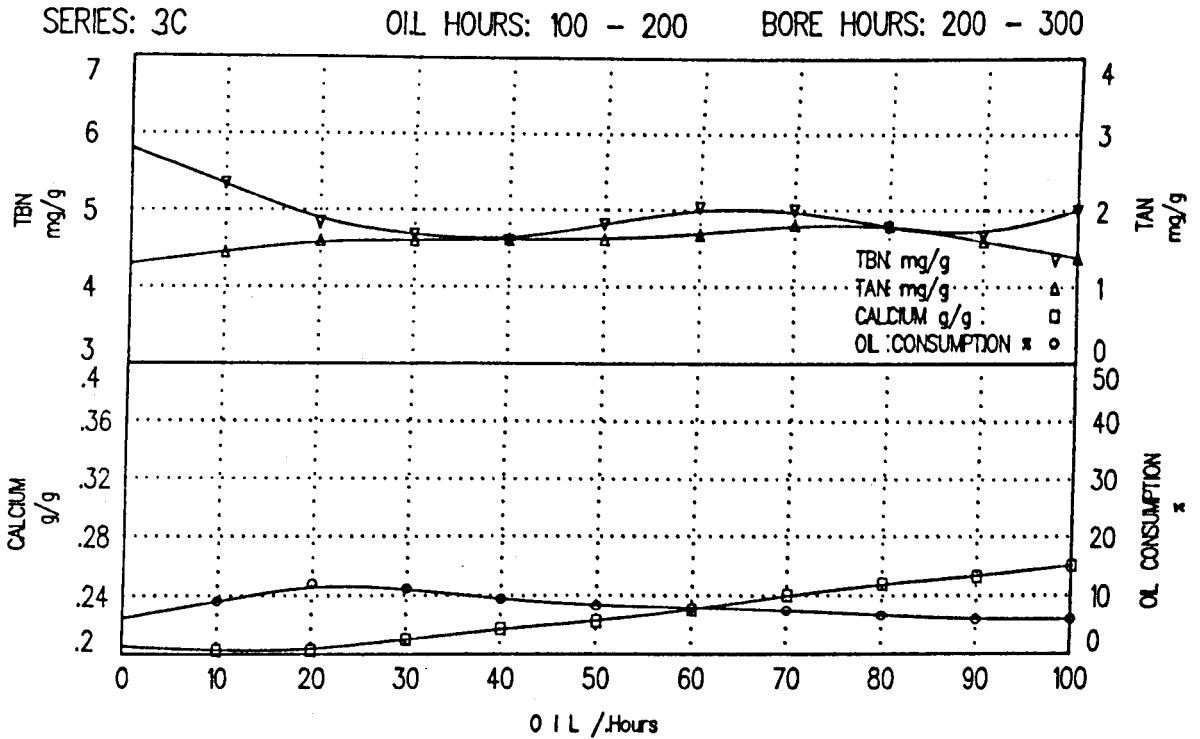
FIGURE 66 (e). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3B).



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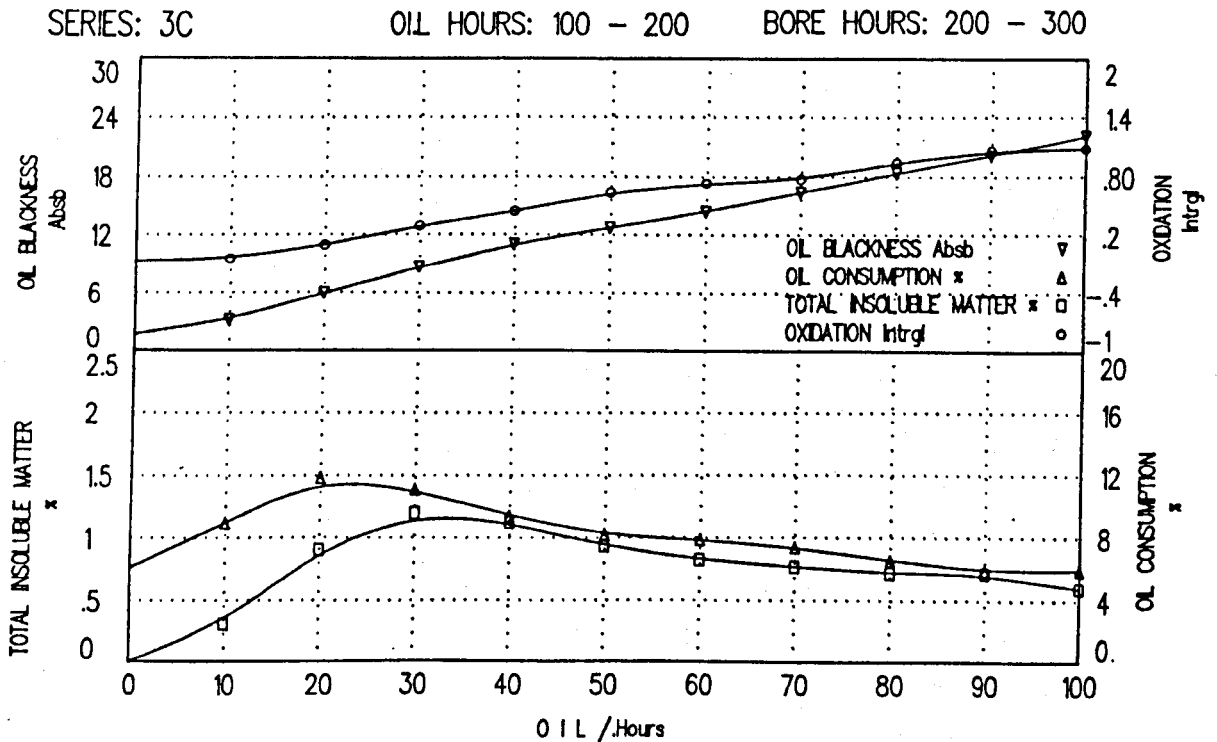
FIGURE 65 (f). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3C).



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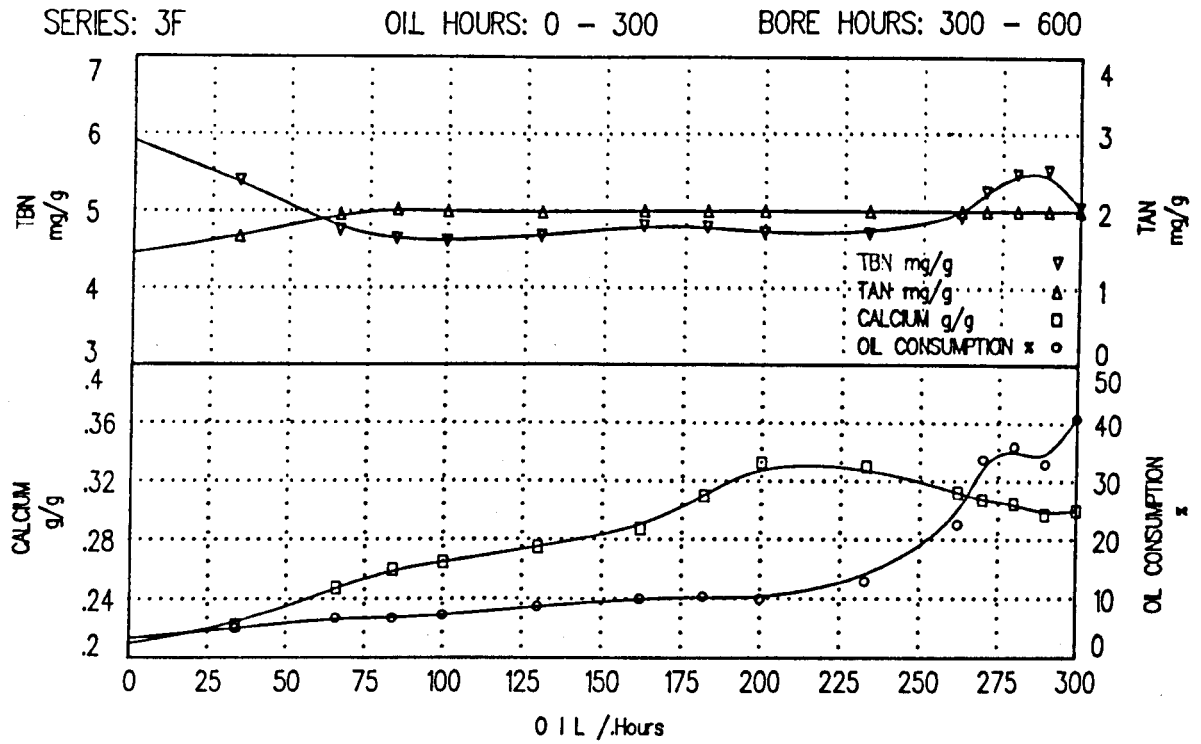
FIGURE 66 (f). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3C).



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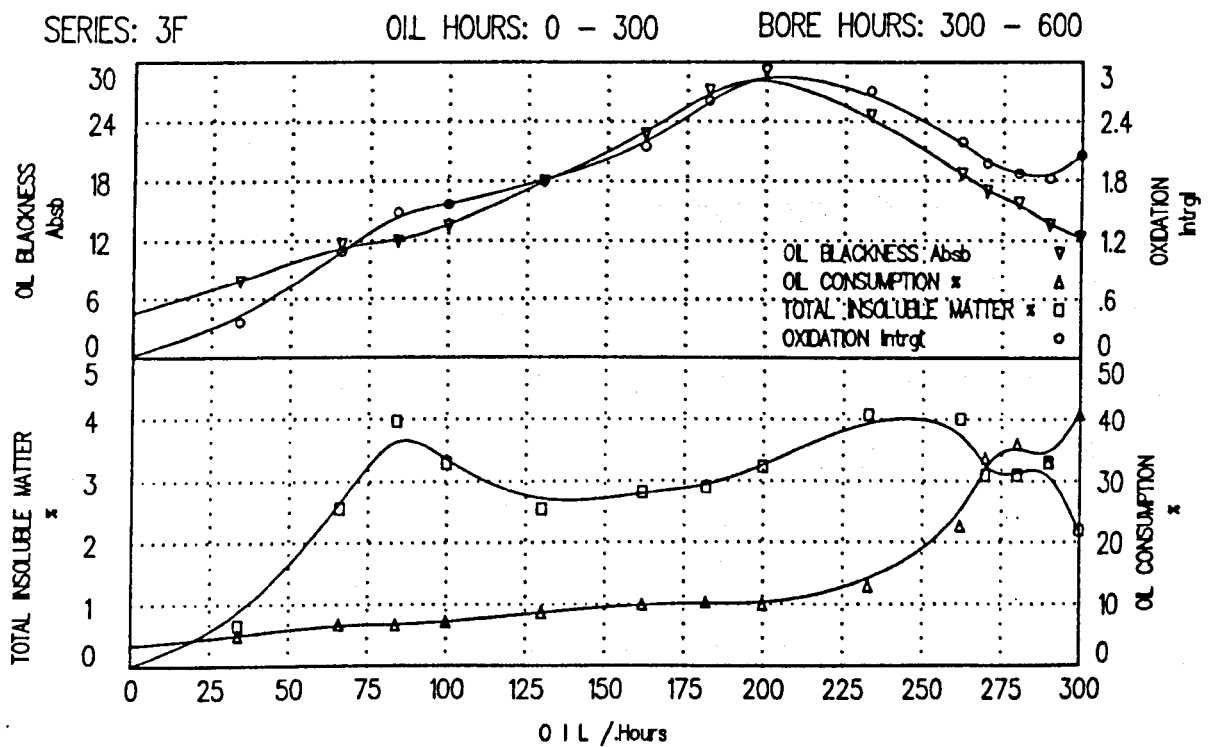
FIGURE 65 (g). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3F).



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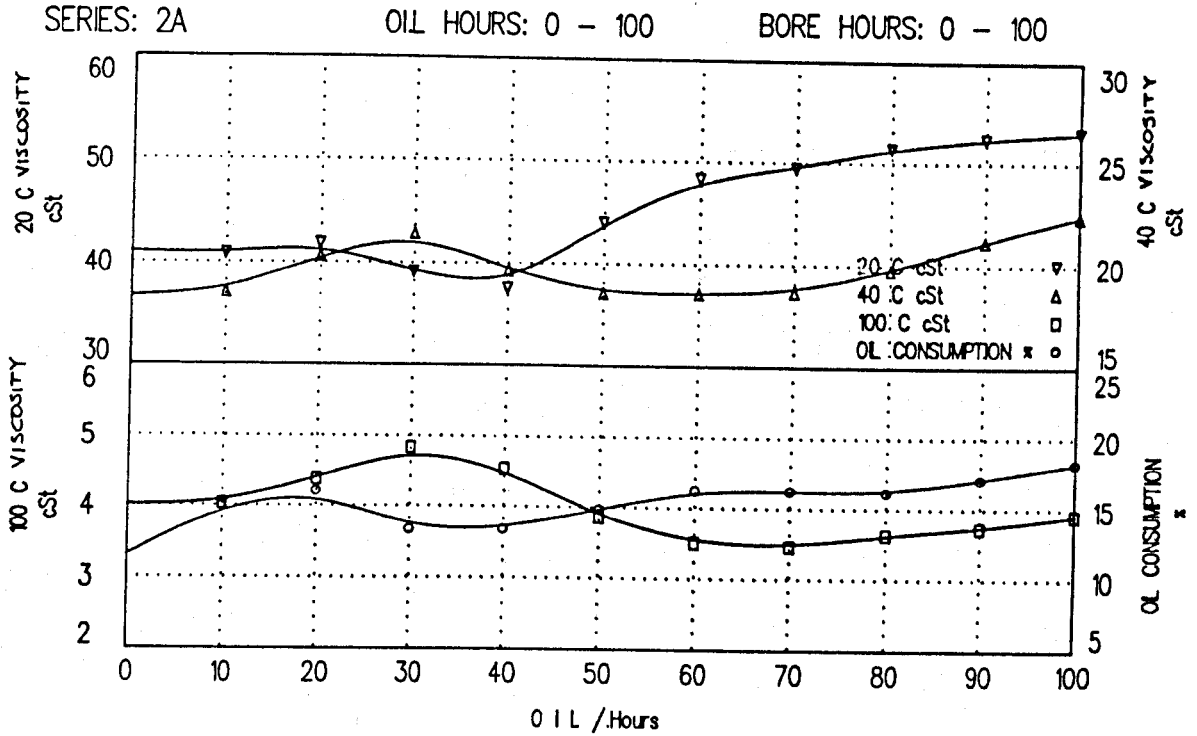
FIGURE 66 (g). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3F).



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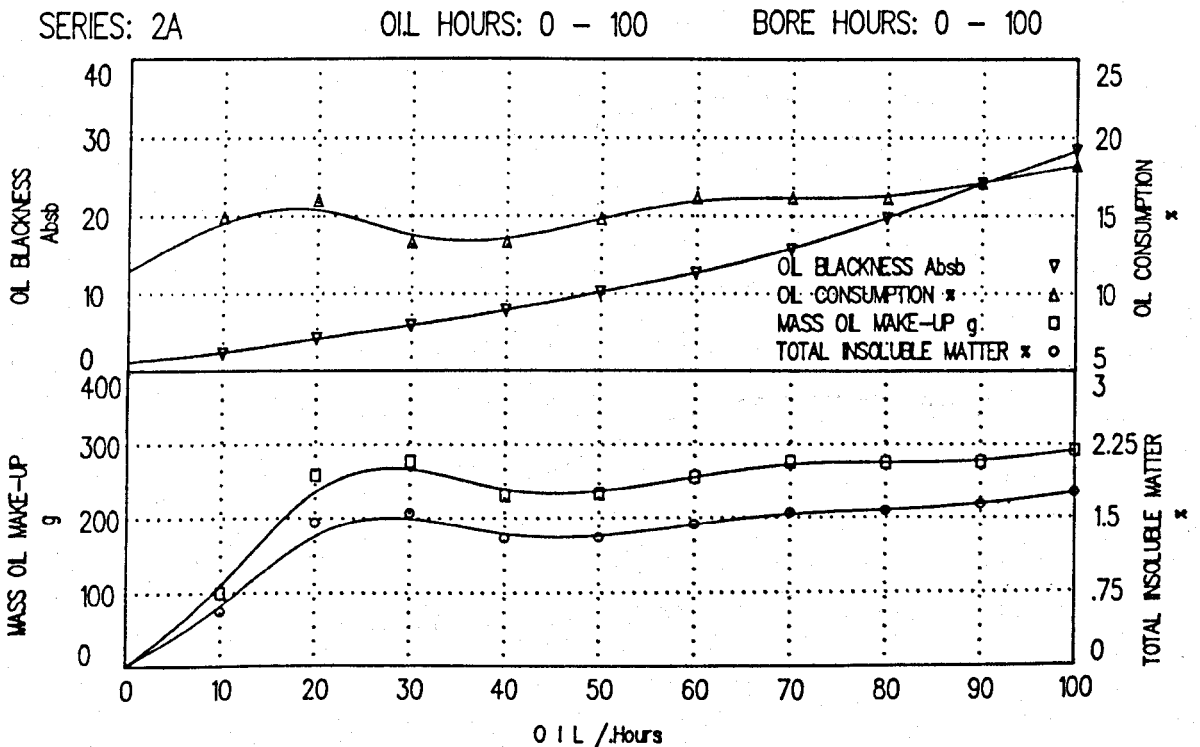
FIGURE 67 (a). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2A).



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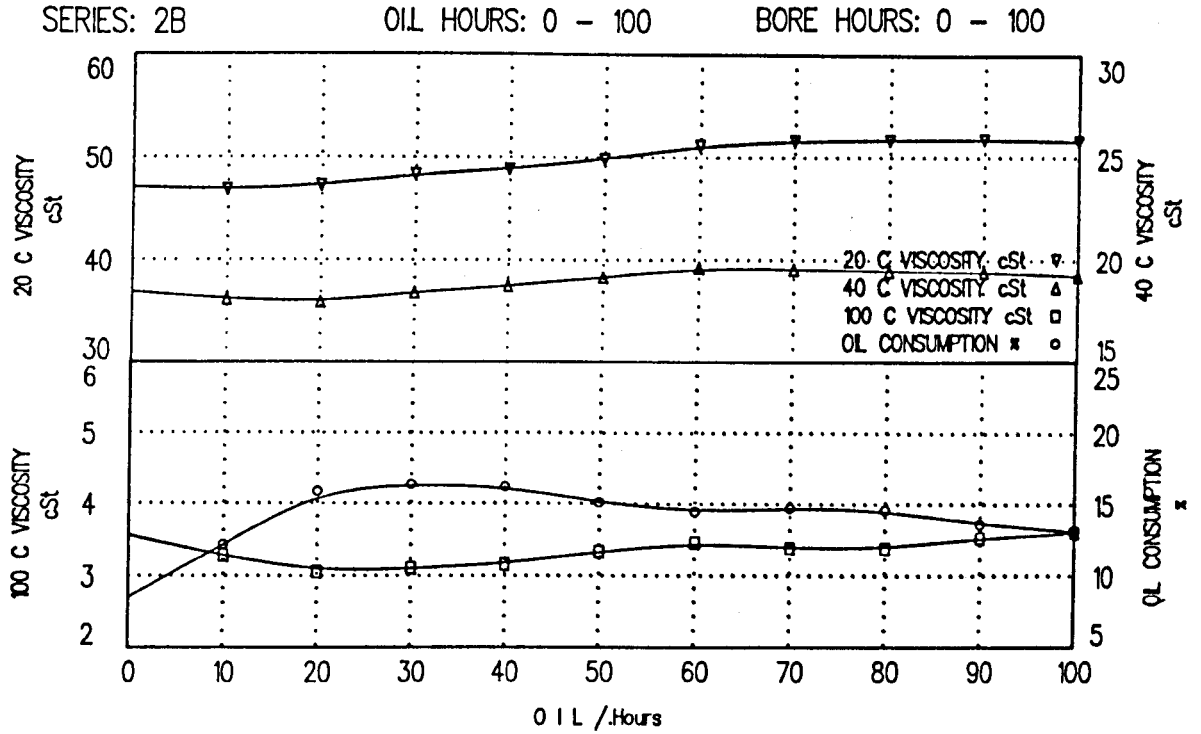
FIGURE 68 (a). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2A).



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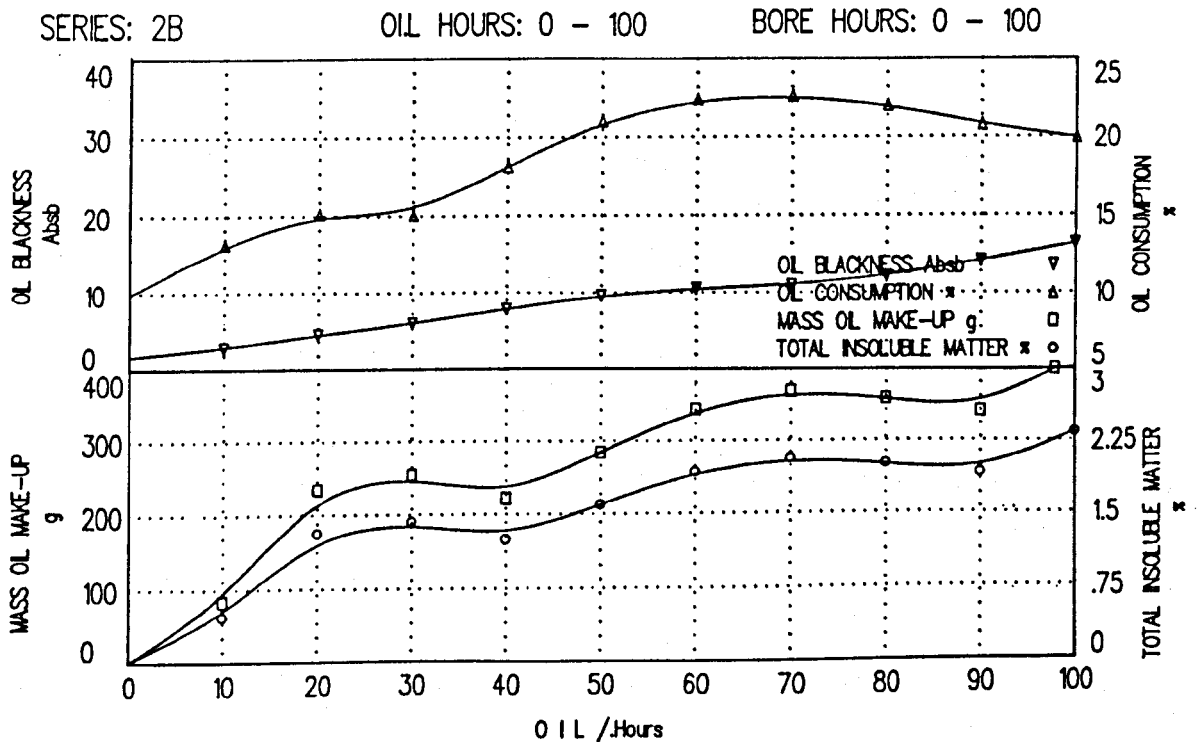
FIGURE 67 (b). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2B).



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FIGURE 68 (b). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2B).

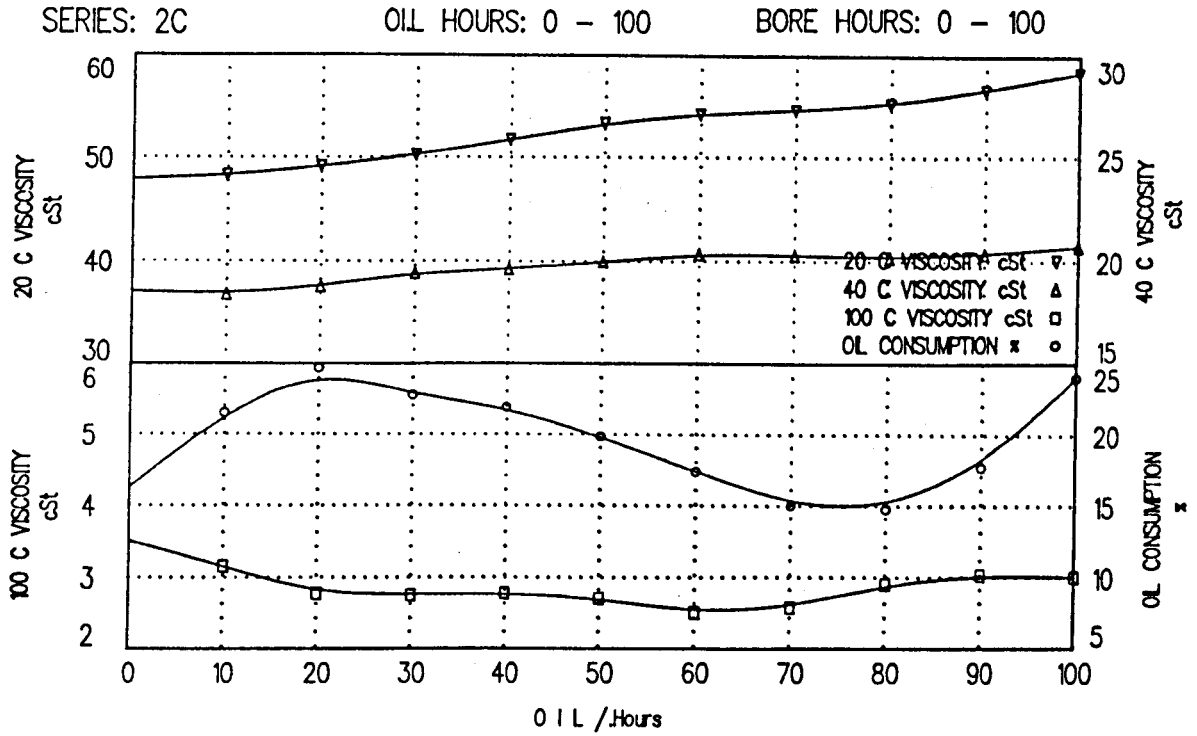


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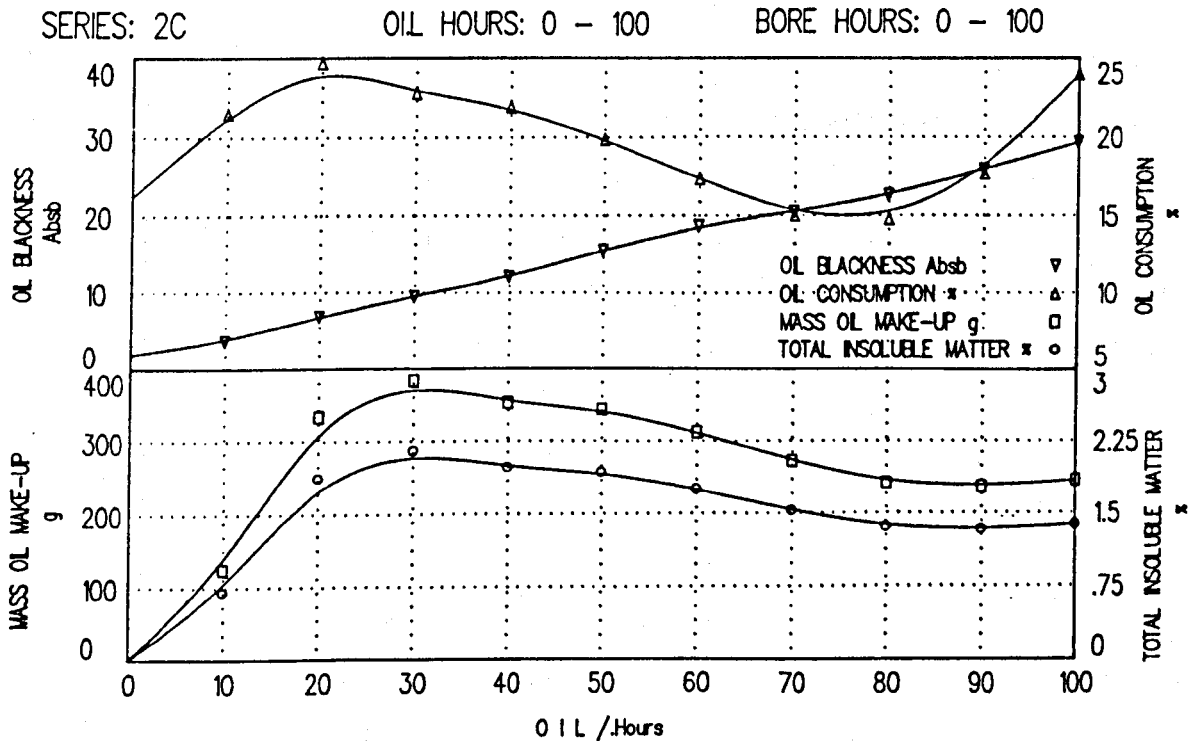
FIGURE 67 (c). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2C).



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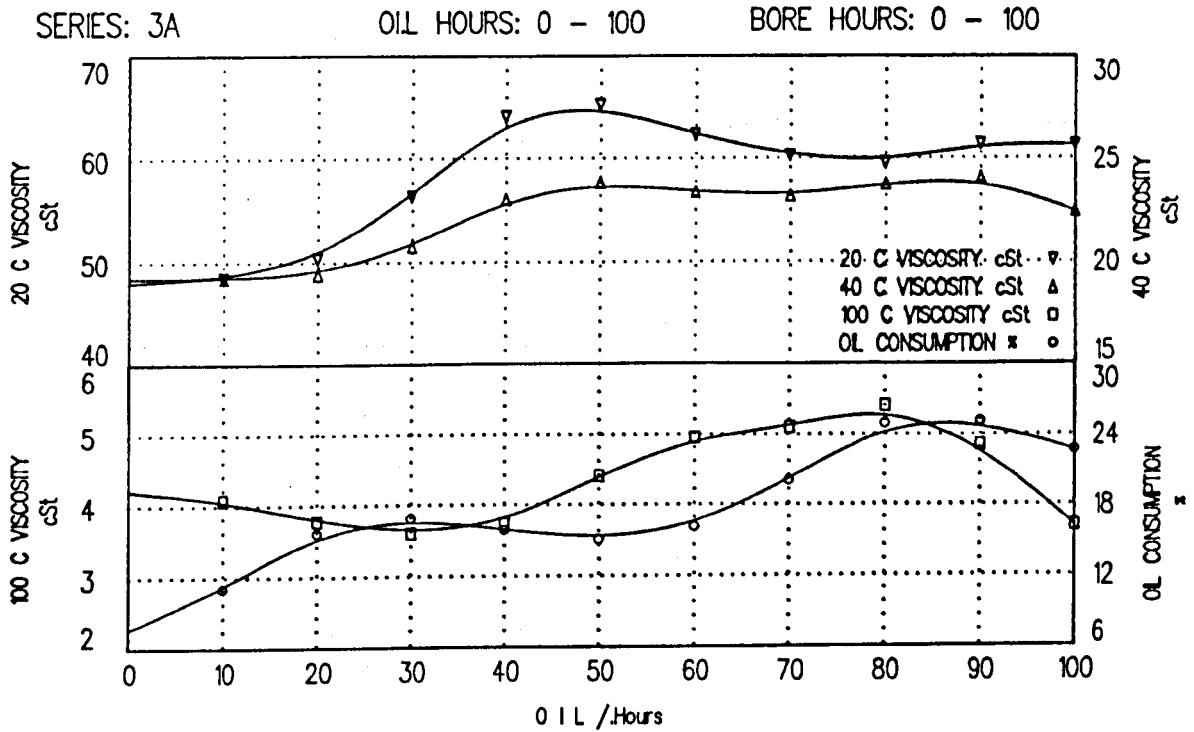
FIGURE 68 (c). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2C).



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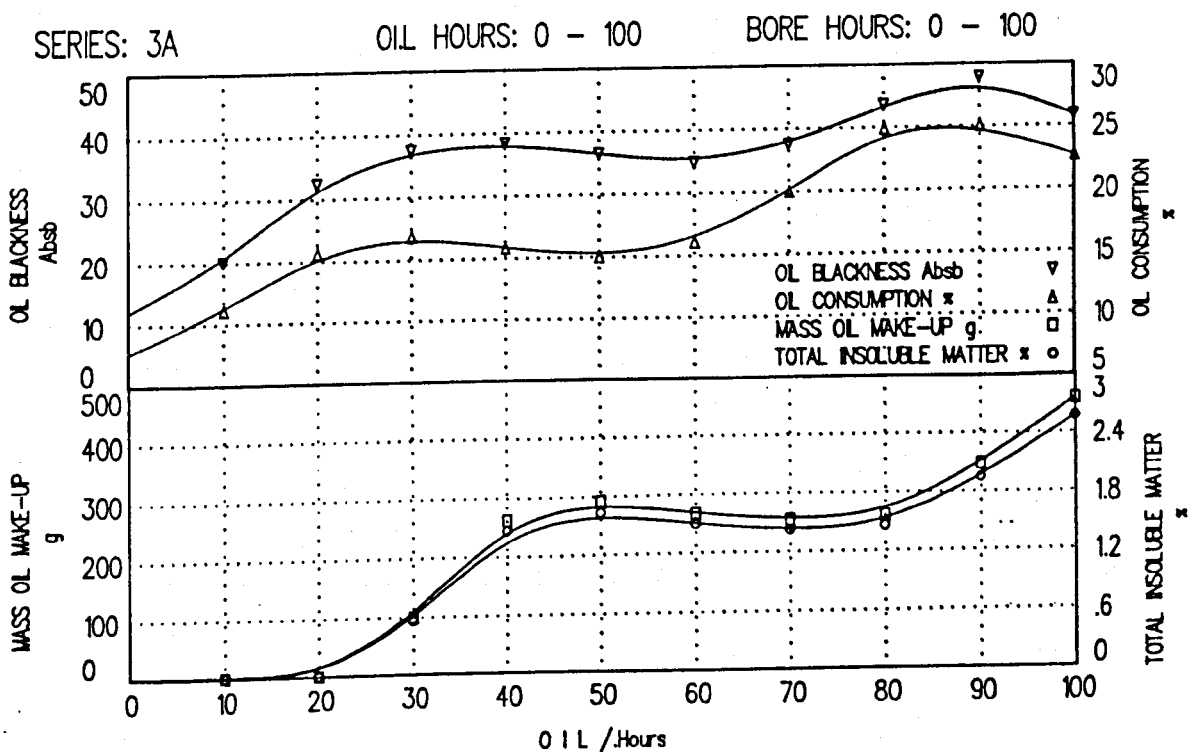
FIGURE 67 (d). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3A).



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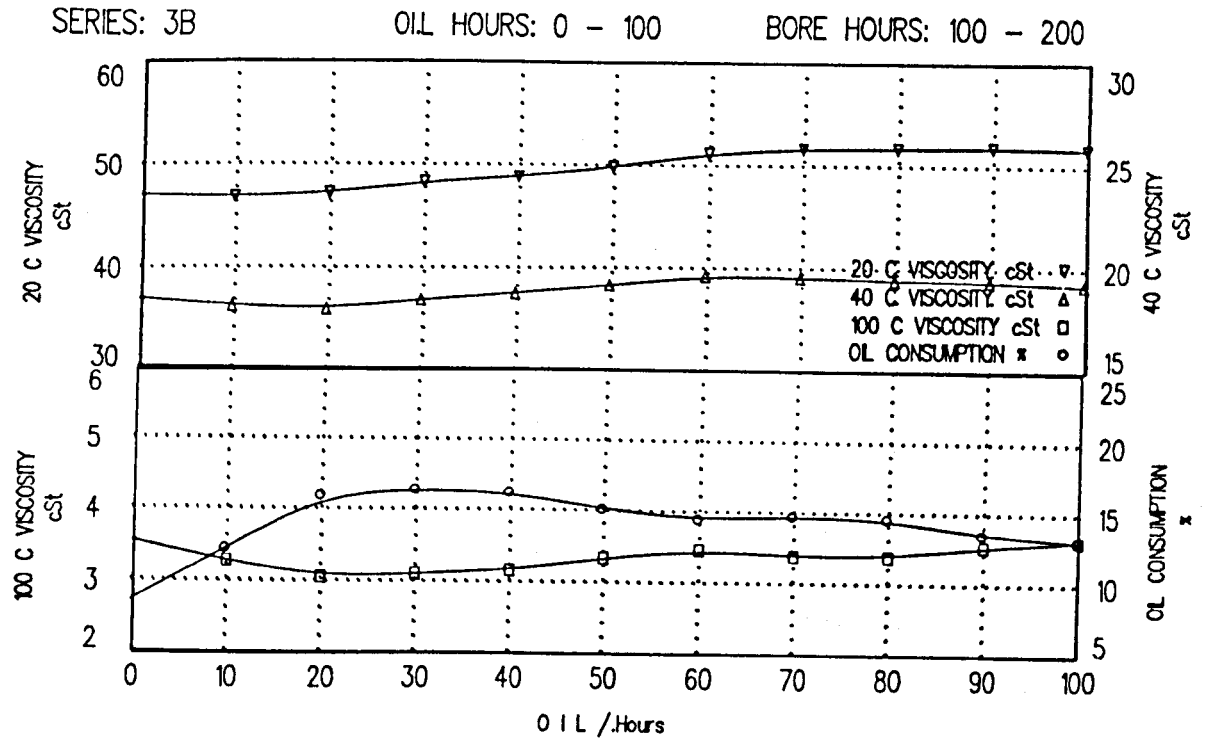
FIGURE 68 (d). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3A).



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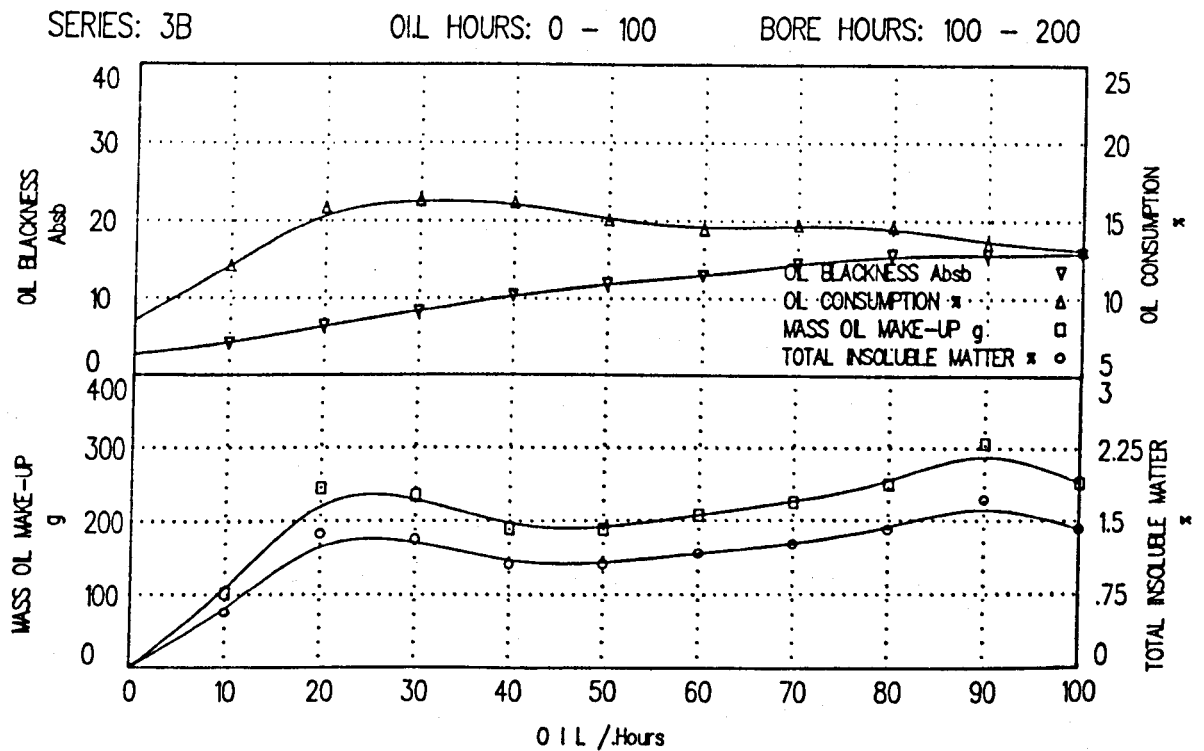
FIGURE 67 (e). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3B).



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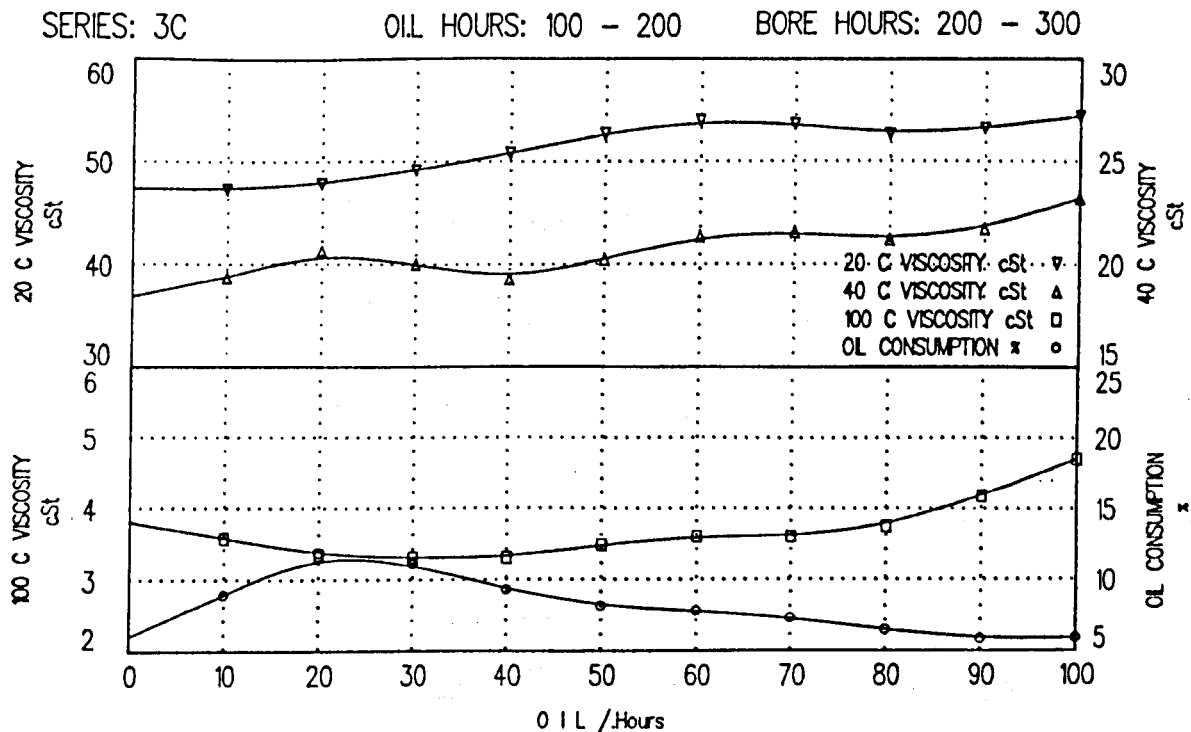
FIGURE 68 (e). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3B).



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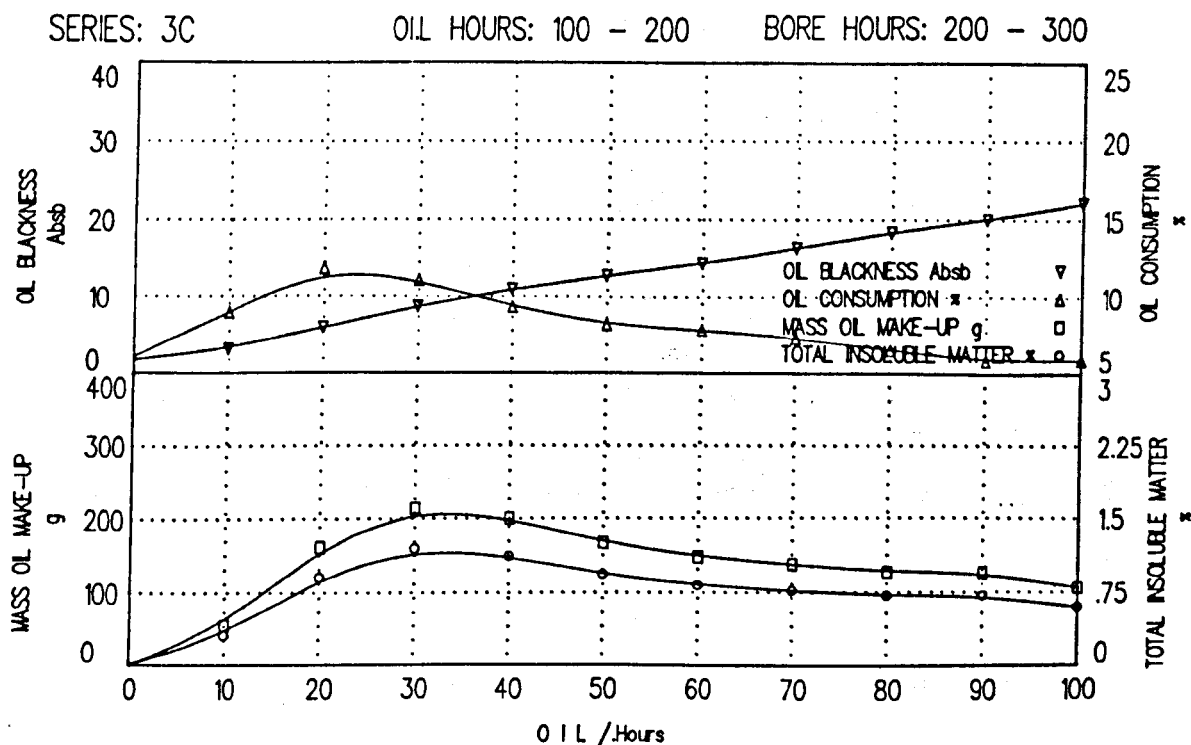
FIGURE 67 (f). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3C).



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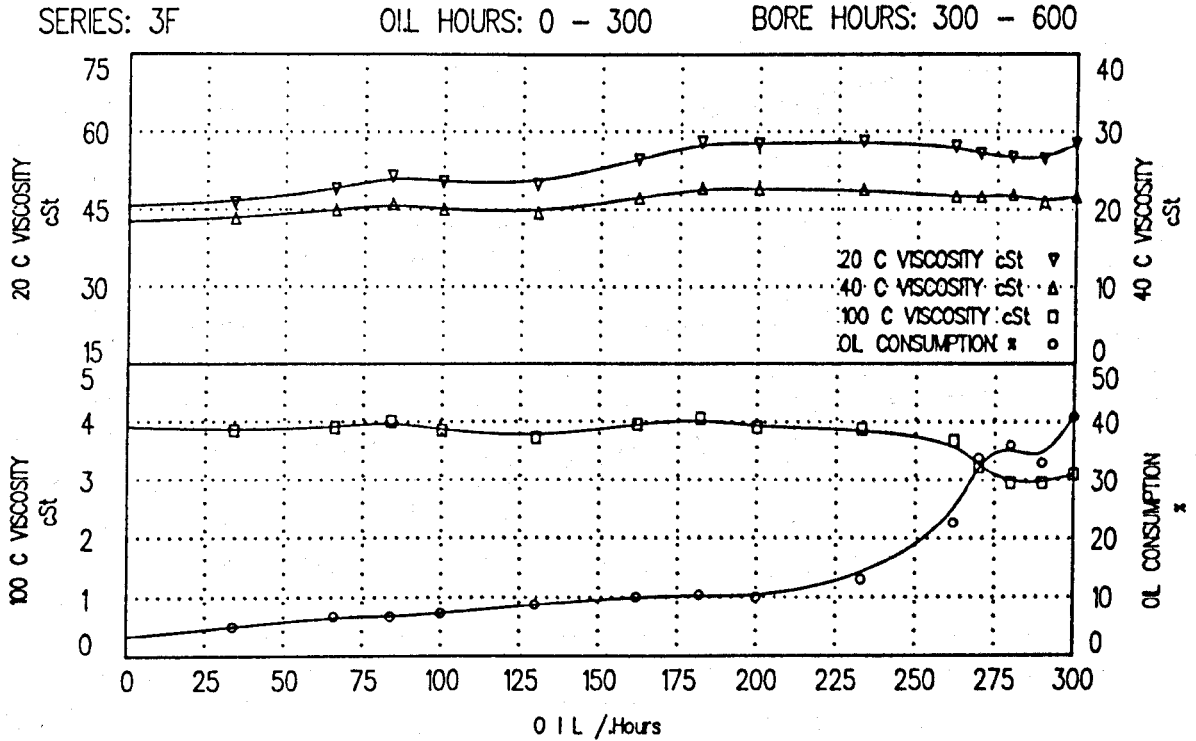
FIGURE 68 (f). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3C).



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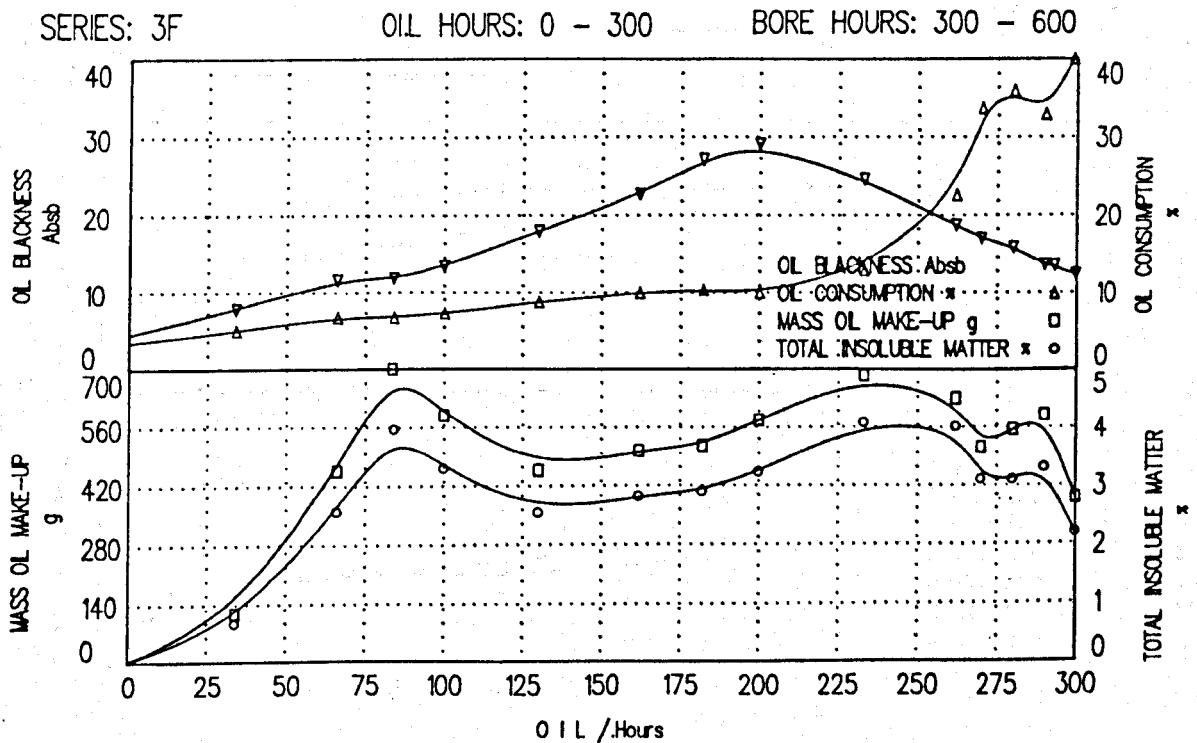
FIGURE 67 (g). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3F).



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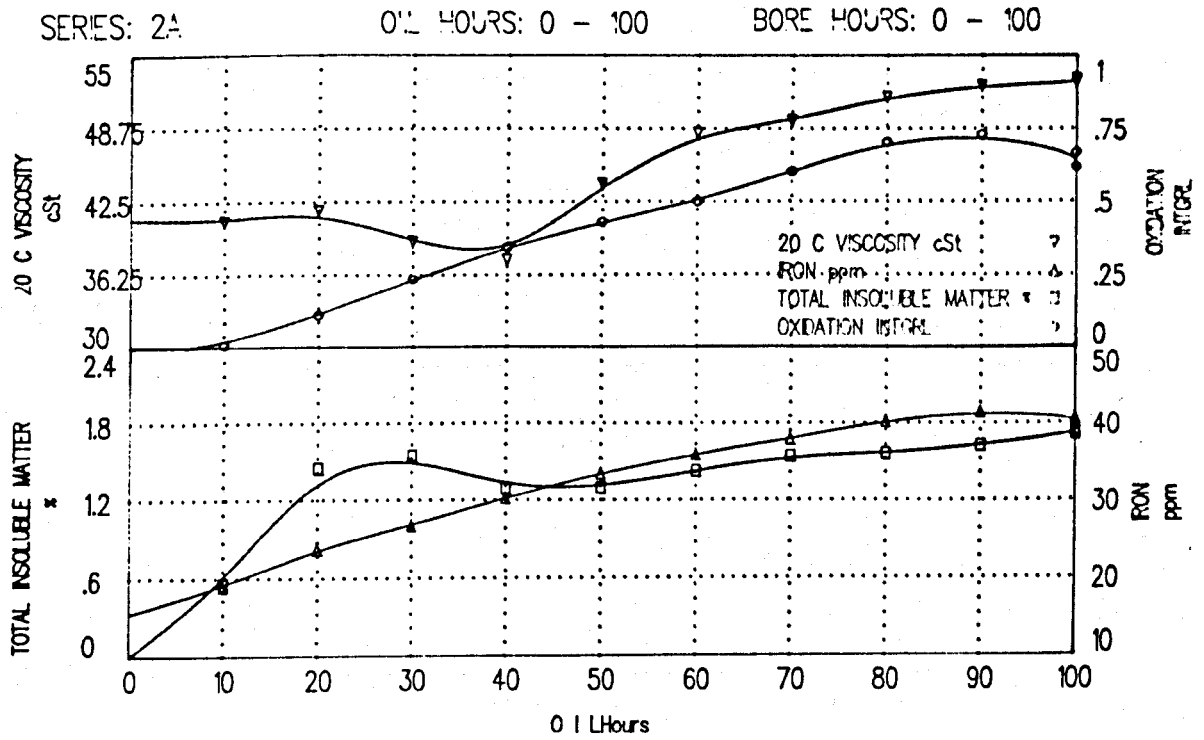
FIGURE 68 (g). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3F).



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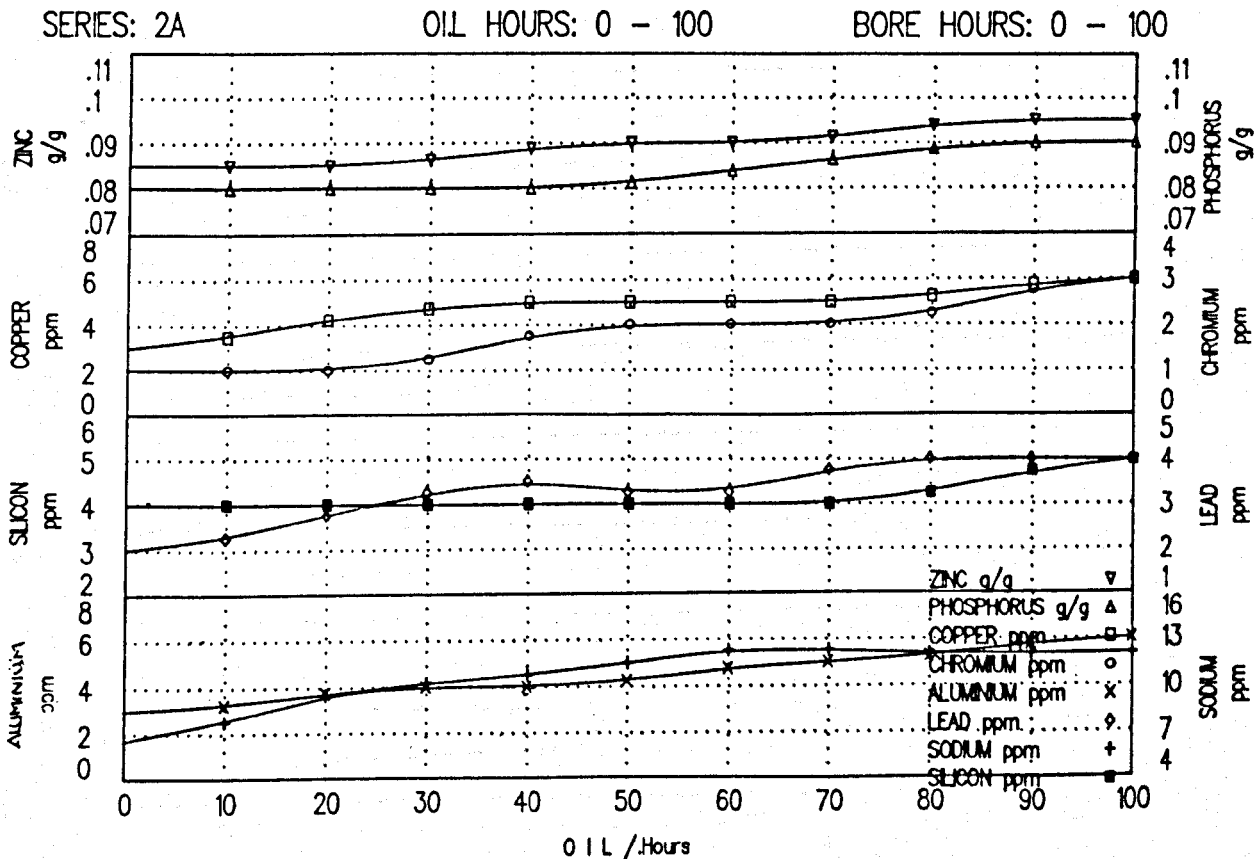
FIGURE 69 (a). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2A).



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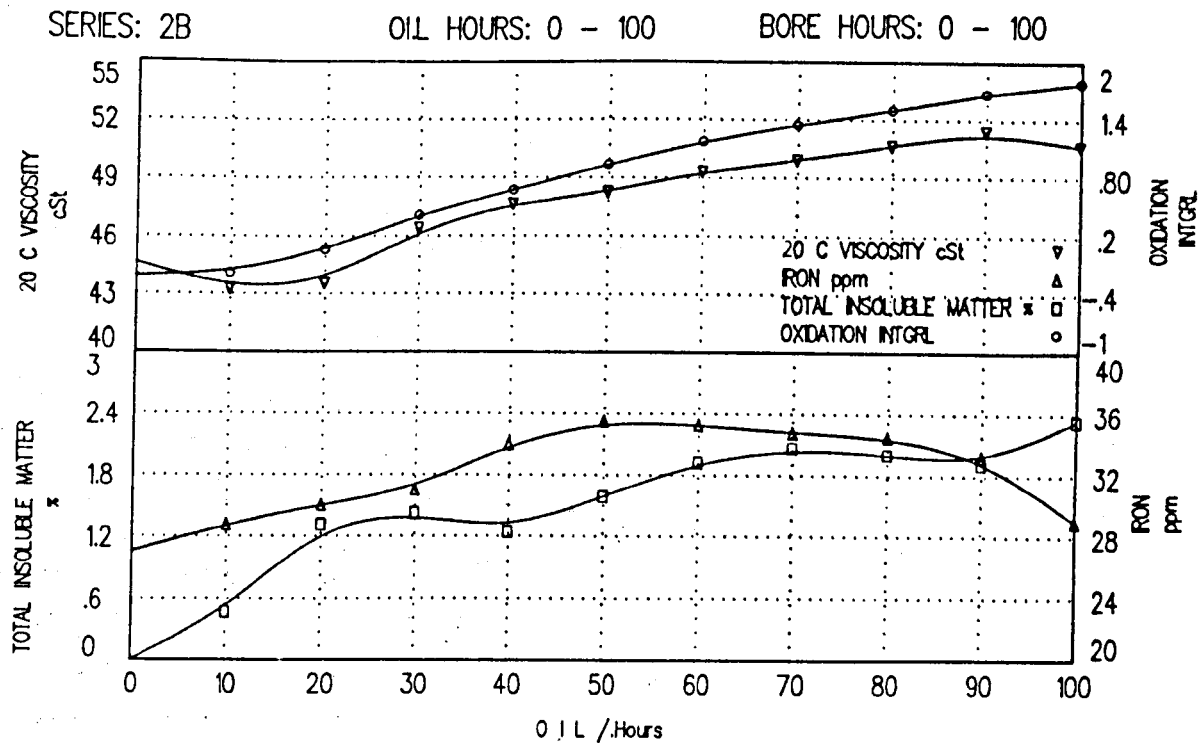
FIGURE 70 (a). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2A).



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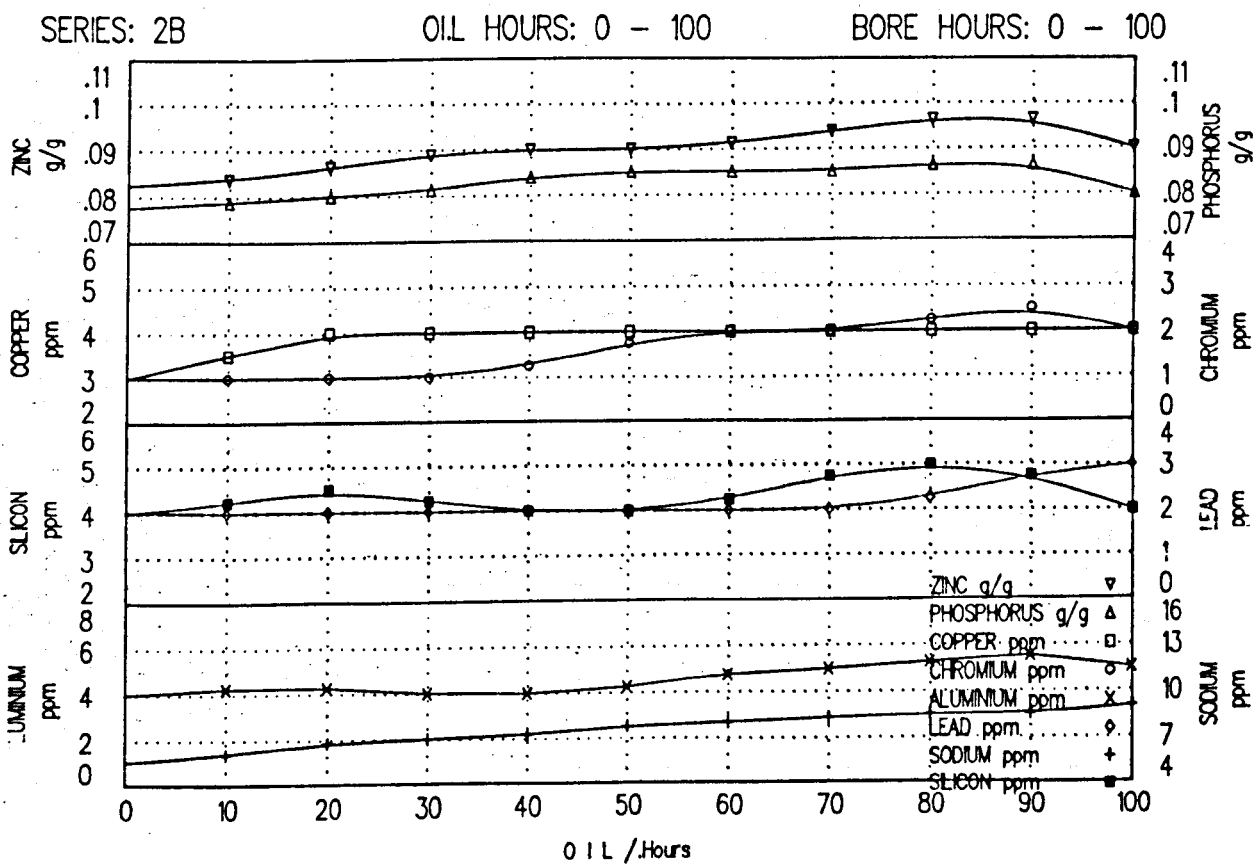
FIGURE 69 (b). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2B).



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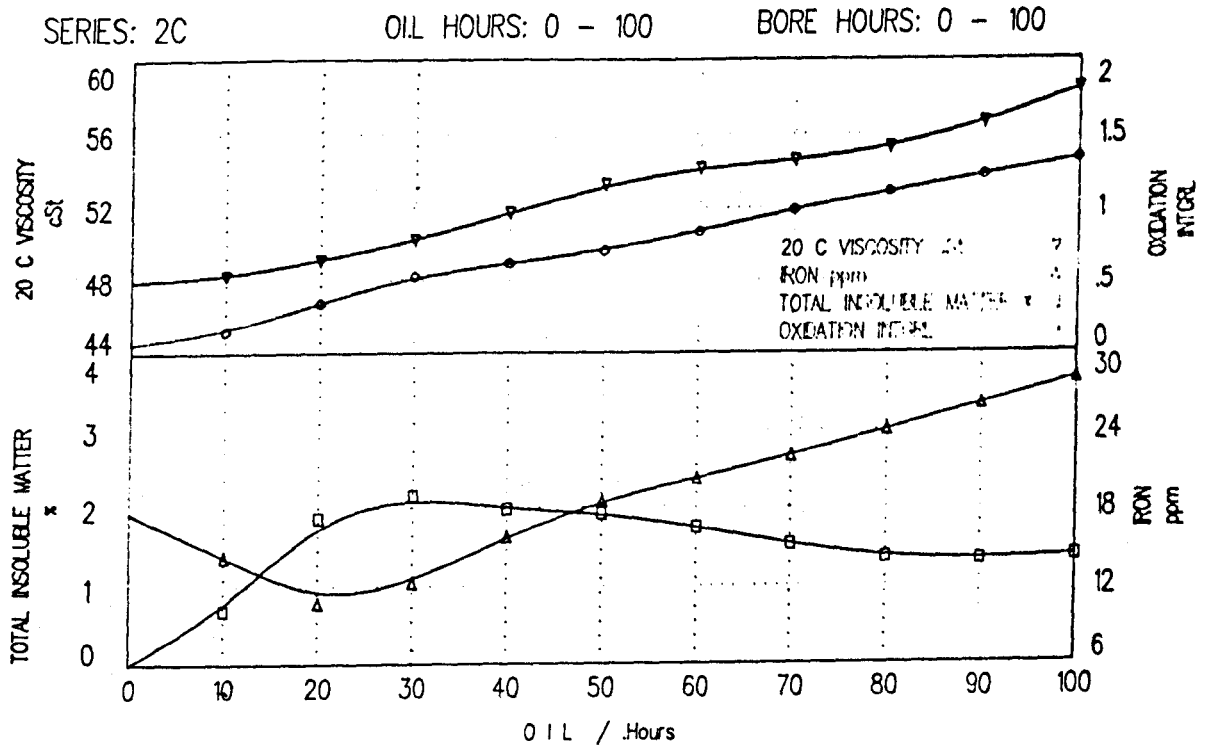
FIGURE 70 (b). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2B).



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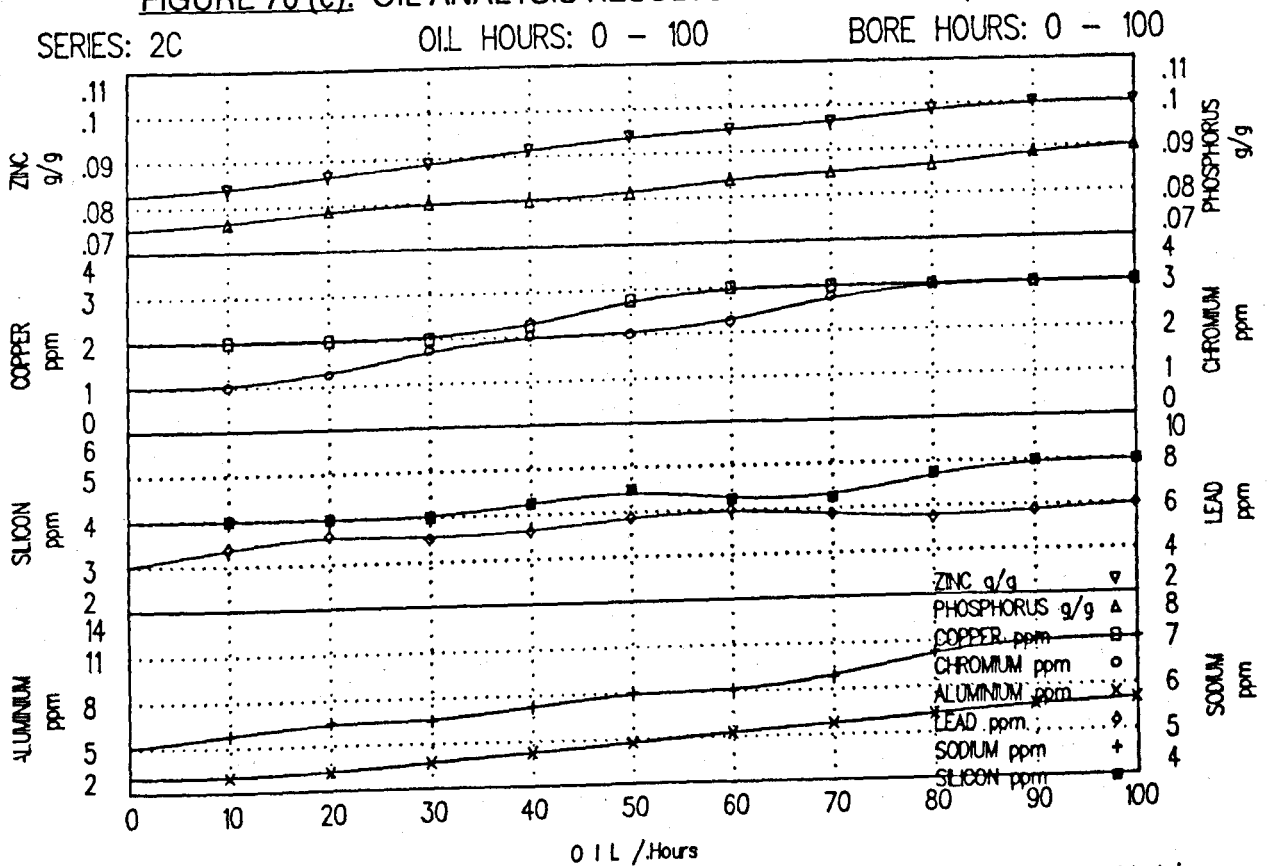
FIGURE 69 (c). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2C).



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FIGURE 70 (c). OIL ANALYSIS RESULTS FOR ENGINE 2 (SERIES 2C).

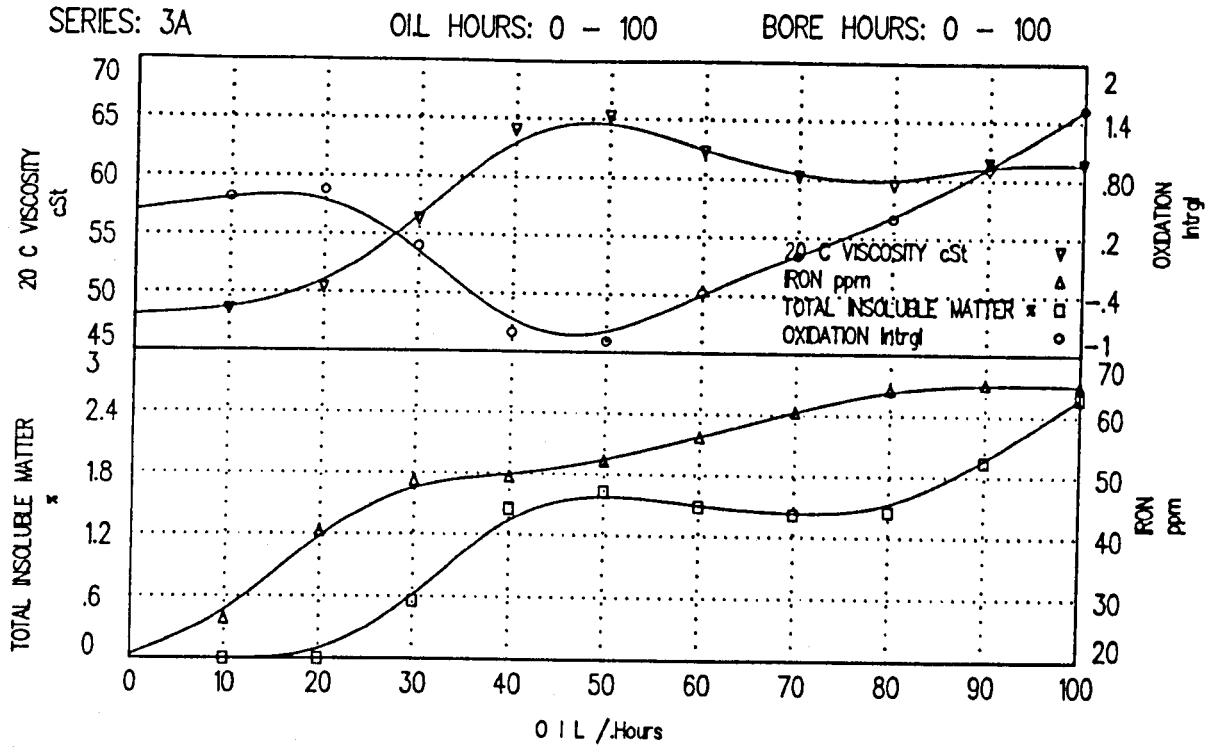


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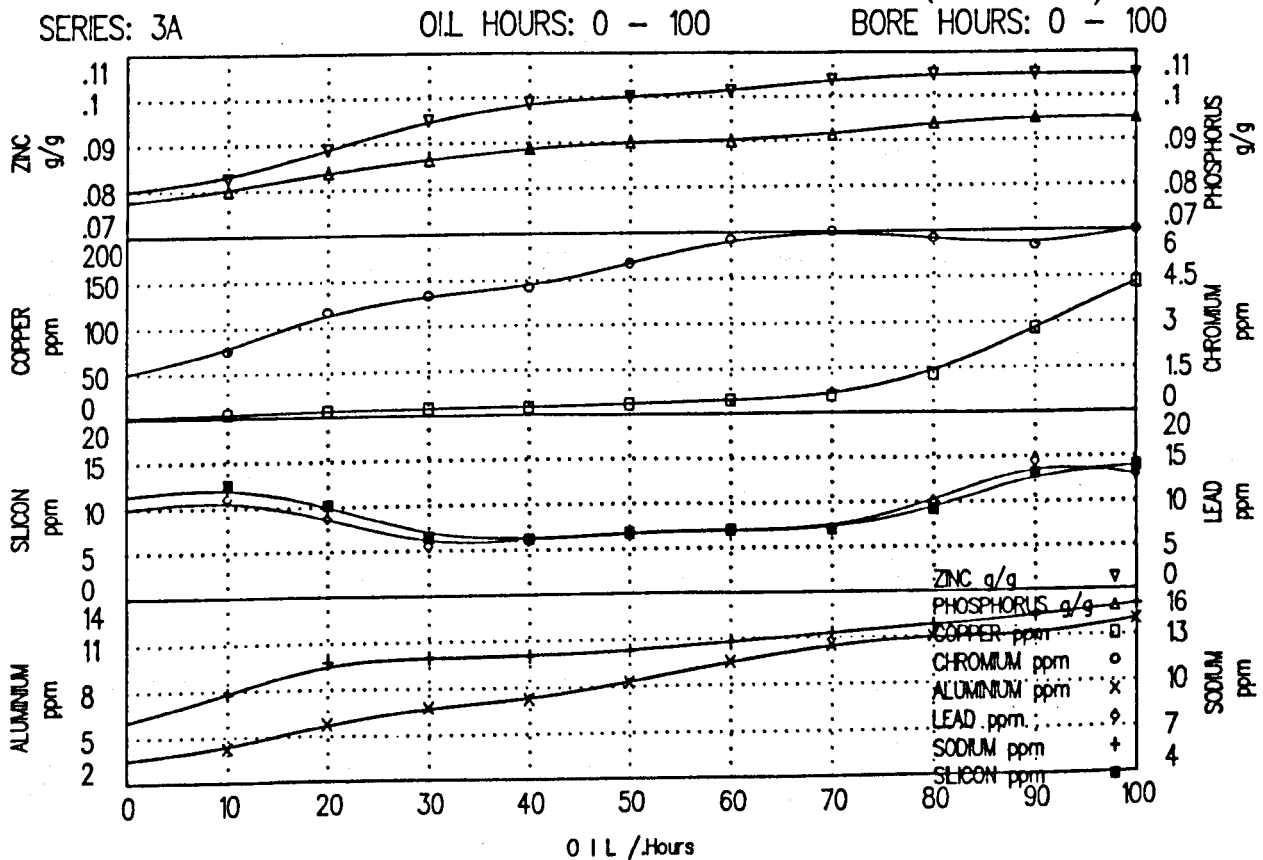
FIGURE 69 (d). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3A).



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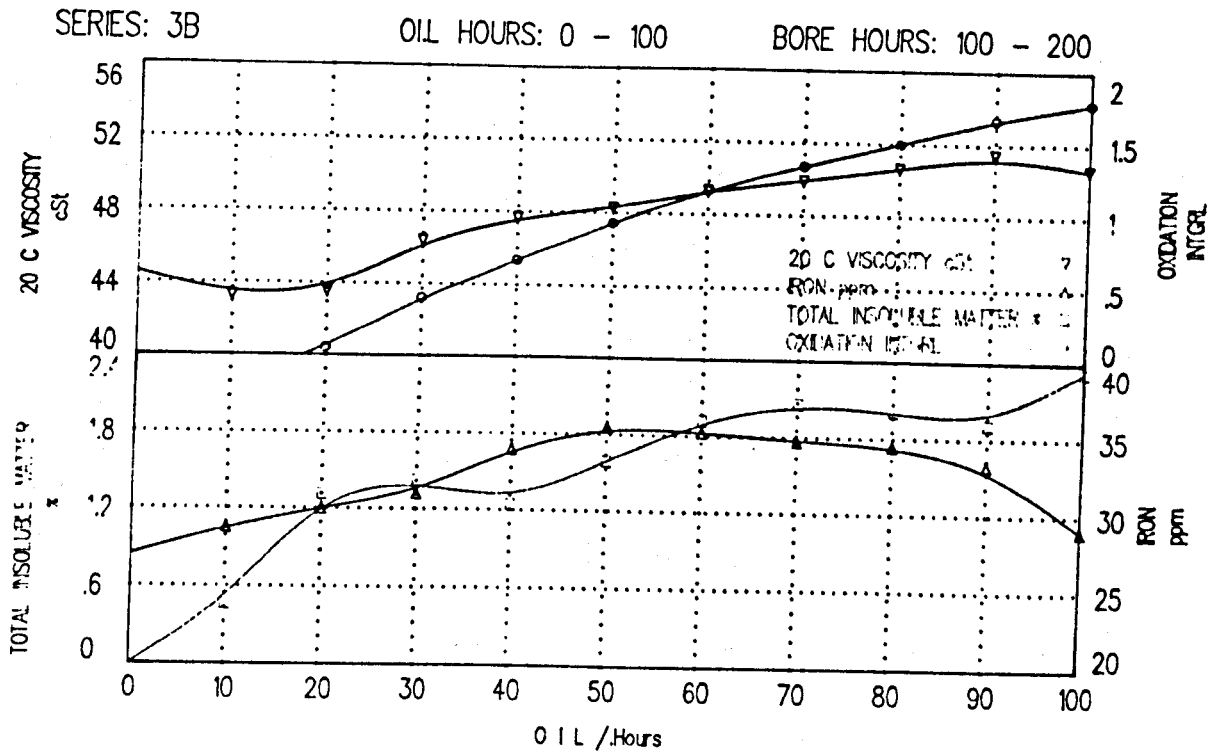
FIGURE 70 (d). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3A).



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**FIGURE 69 (e). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3B).**



**FIGURE 70 (e). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3B).**

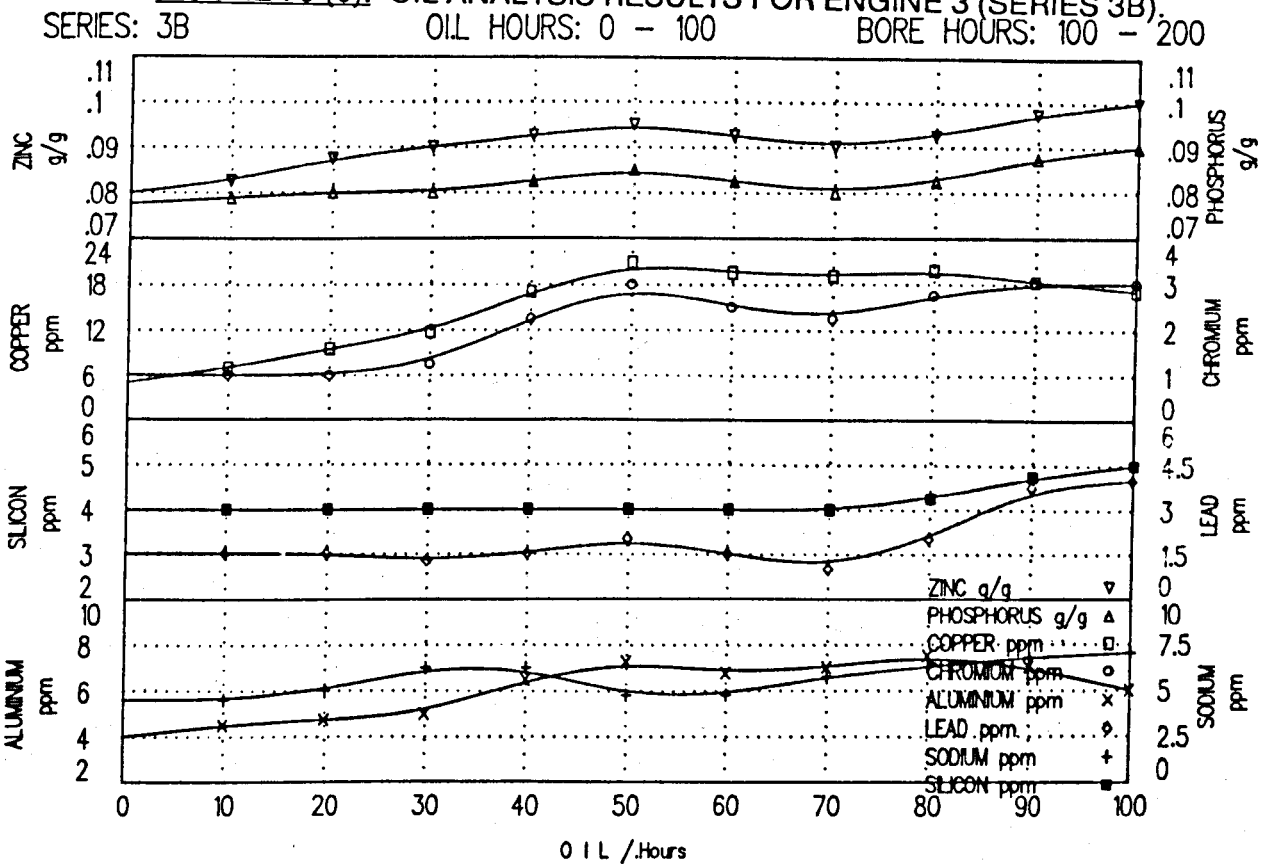
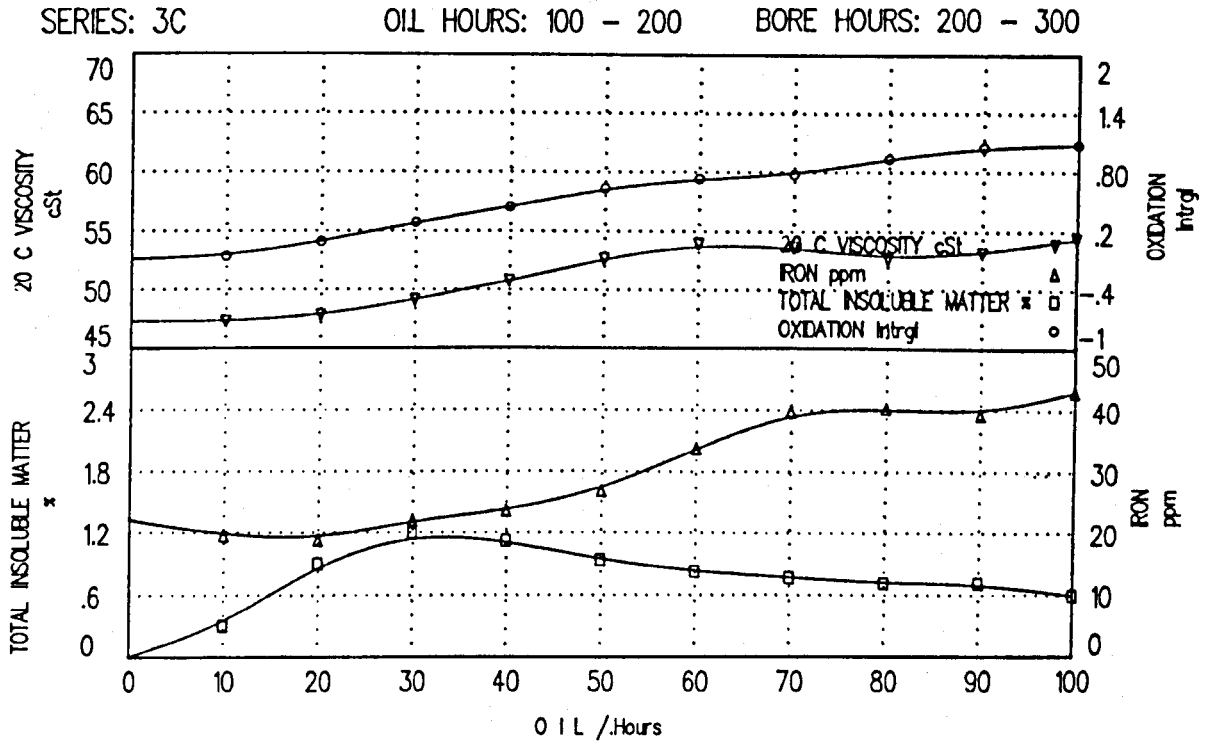


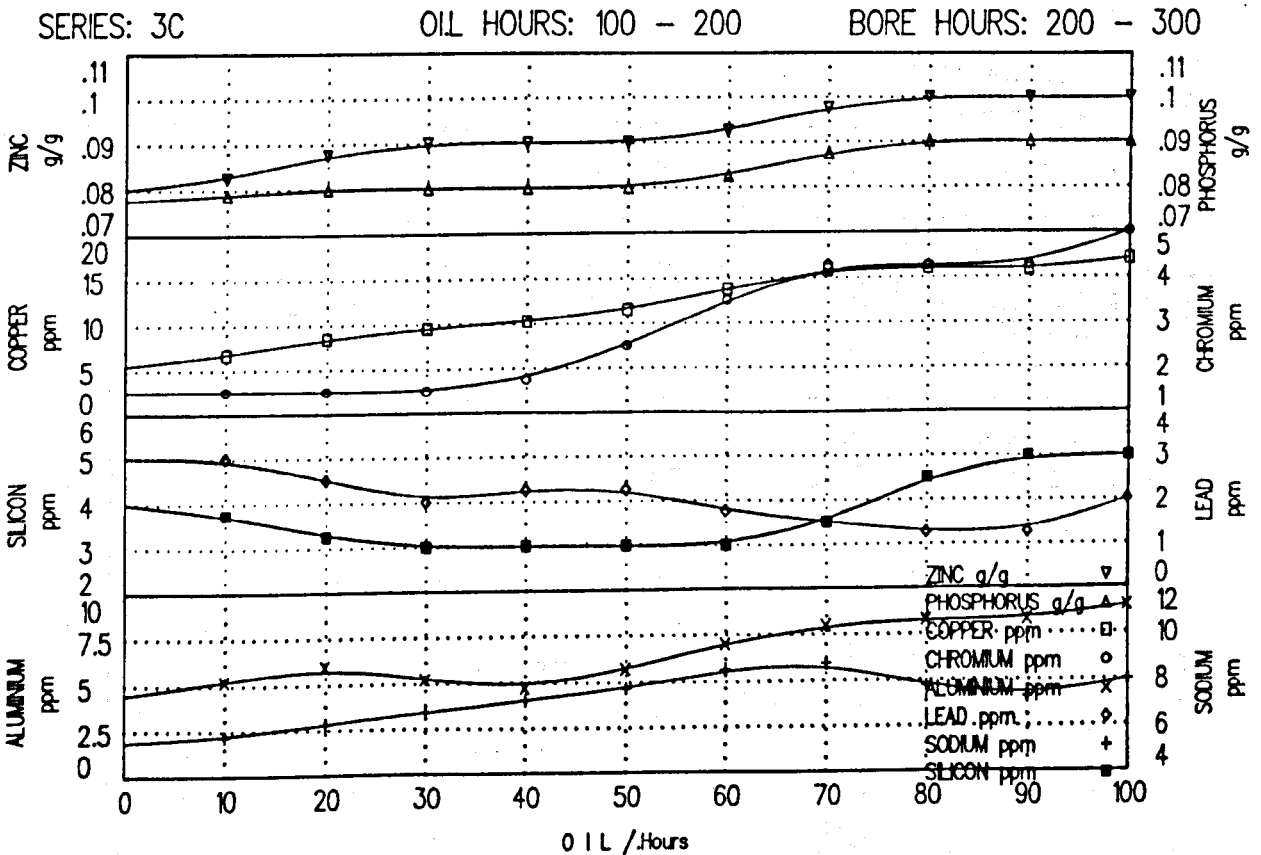
FIGURE 69 (f). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3C).



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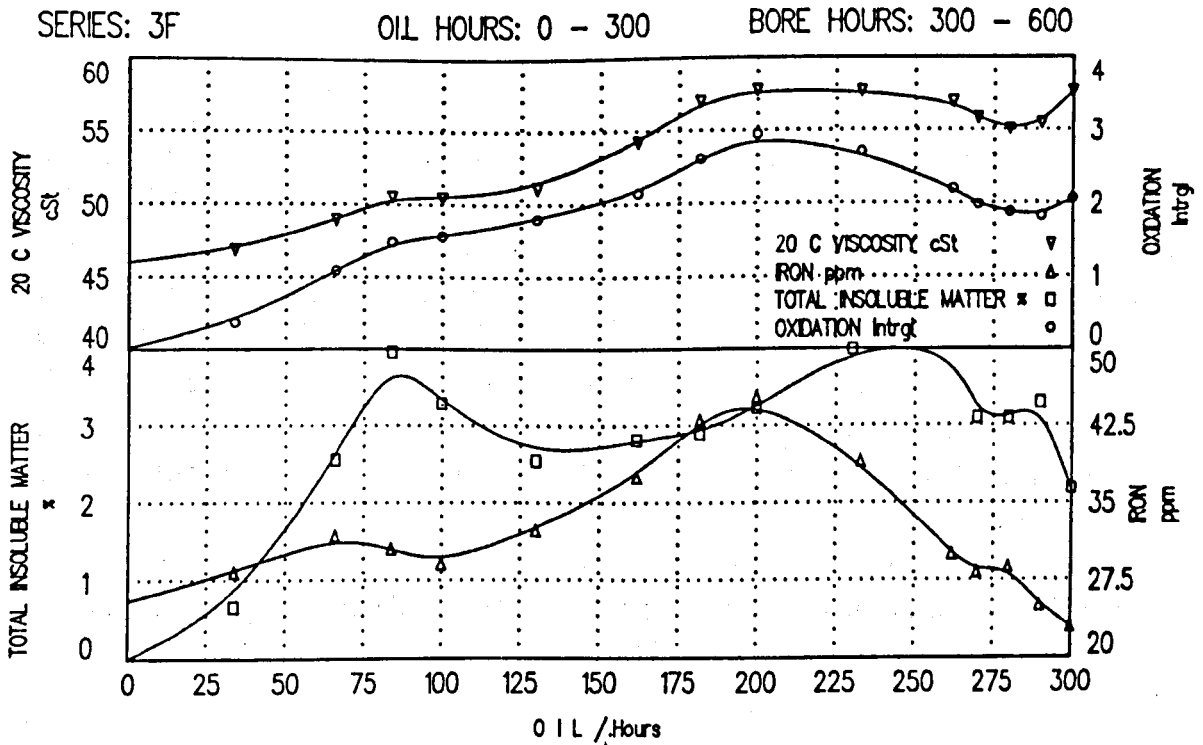
FIGURE 70 (f). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3C).



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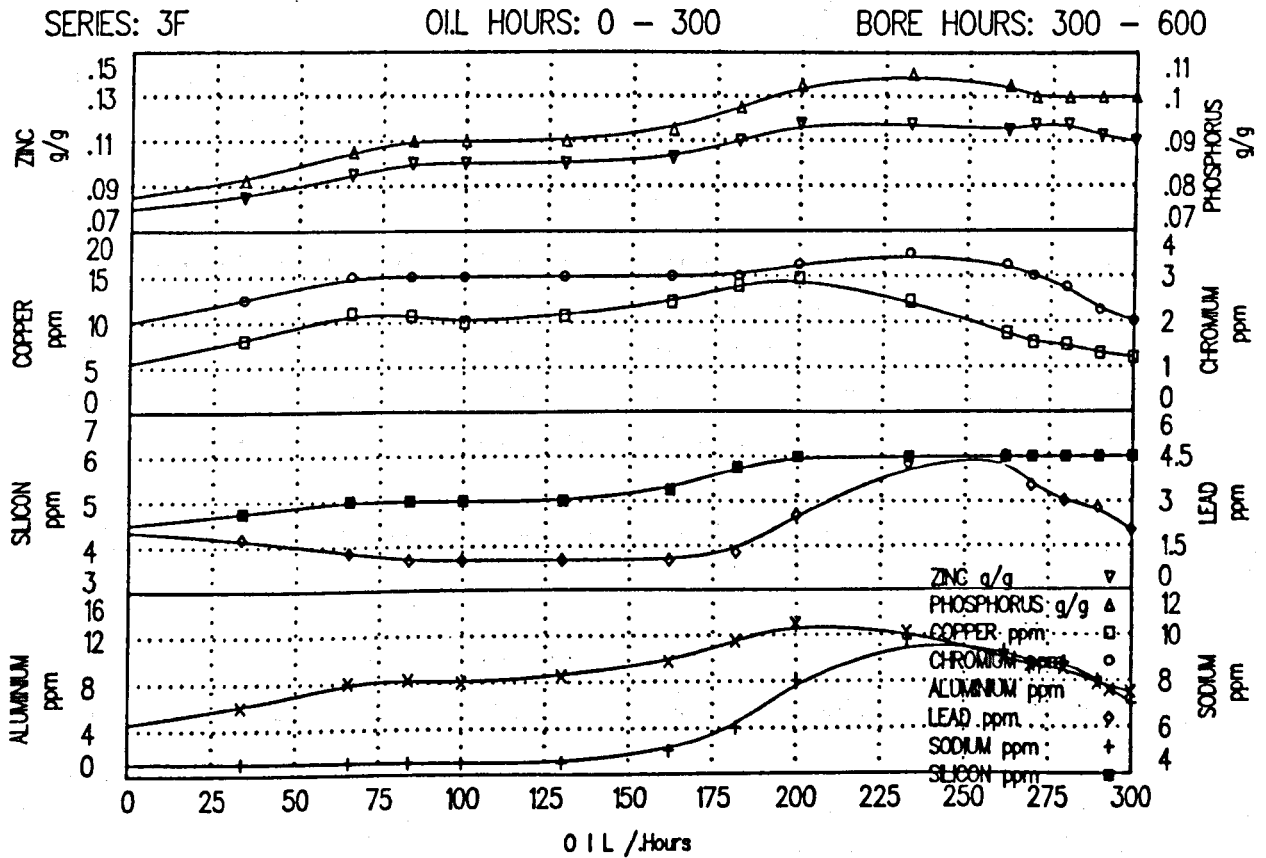
FIGURE 69 (g). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3F).



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FIGURE 70 (g). OIL ANALYSIS RESULTS FOR ENGINE 3 (SERIES 3F).



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its removal from the bulk used oil. Neither of these two removal mechanisms would be likely for the highly cationic nature of calcium.

#### 4.9.8 Total Acid Number.

The Total Acid Number appears to increase initially and then stabilise at a constant 2.5 mg KOH/g after about 40 hours of testing. The new oil has a TAN value of 1.3 mg KOH/g. Just like the TBN values, therefore, the TAN value does not appear to represent a wholly true measure of the acidity of the oil. The TAN values stabilise at about the same time that the TBN values stabilise. All that can be deduced from this is that the conclusion drawn from the rapid decline in TBN is confirmed by the opposite characteristics of the TAN values. That is, the TAN and TBN trends do conform to the same theory of new formulated oils having acidity/alkalinity values that are over-estimates of the true values. An alternative reason for the stabilisation of the TAN values is that the TBN of the make-up oil is sufficient to neutralise the acids produced during that time interval before the next top-up. This reason would be most unlikely considering the arguments discussed in section (4.9.1).

#### 4.9.9 Trend Analysis from Parameter Cross-plots.

The trends that were found on studying the various oil parameters in the sections above were cross-plotted, that is, one parameter was plotted against another parameter, instead of the test time. This method of analysis reveals the inter dependence of the parameters. Each of the plots that showed some sort of inter-dependence is discussed below:

##### 4.9.9.1 Total Insoluble Matter versus Oil Make-up.

The plot of Total Insoluble Matter against the amount of Oil Make-up, Figure 71, shows a linear inter-relationship between these two parameters. The gradient of this plot (TIM/Make-up) was found to be 3.1/550 (%/g). This indicates that the percentage TIM increases at a fixed rate, dependent only on the oil consumption level. The build-up of TIM may be the result of the selective combustion of the base oil's light fraction. The dilution of the used oil by addition of fresh oil will, therefore, lower the TIM levels by an amount dependent upon the oil-make level.

##### 4.9.9.2 Zinc and Phosphorus versus Calcium.

The plot of Zinc against Phosphorus, Figure 72, shows an almost 1:1 relationship. This indicates that both these elements are involved in the same chemical reactions and

products. The plots of these two elements, Zinc and Phosphorus, against the calcium levels shows two slightly different inter-relationships, Figures 73 and 74, respectively. The three elements are derived from the additive package, in an atomic proportion of Calcium:Zinc:Phosphorus of 4.2:1:2, in the new oil. In the used oil, the atomic proportions of these three elements changes to 4.6:1:1.9. This indicates that the calcium accumulates at a different rate than those of either phosphorus or zinc. The calcium, as mentioned in the previous section, is not removed selectively from the oil. On the other hand, both zinc and phosphorus undergo some additional interaction due to the chemical nature of ZDDP, from which they are derived, namely reaction with the iron of the cylinder bore. The minute difference in the proportion of zinc and phosphorus levels in the used oil indicates that phosphorus forms new compounds with the iron of the cylinder bore and/or is removed through combustion, whereas zinc is not.

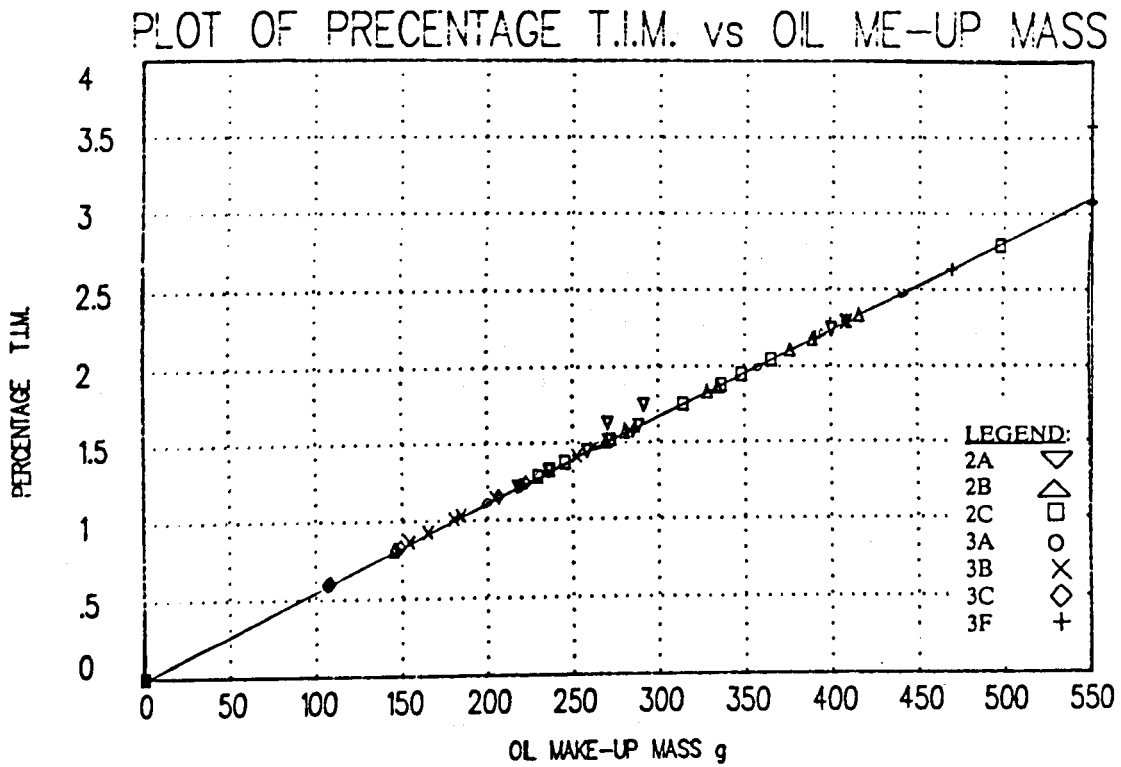
#### 4.9.9.3 Calcium versus Oxidation.

The plot of calcium versus oxidation of the oil indicates a linear relationship between these two parameters, the gradient of the slope being 0.05 (g calcium/oxygen integral), Figure 75. This trend indicates that calcium forms complexes with oxygenated compounds, similar in structure to those of the calcium over-based soap constituents of the TBN compounds. This is likely due to the cationic properties of calcium in an organic medium which is otherwise non-polar in nature. The trend also indicates that calcium does not constitute reactive TBN to keep oxidation in check.

#### 4.9.9.4 Total Acid Number versus Oxidation.

The plot of Total Acid Number against the oxidation level, Figure 76, indicates a linear variation of the former with the latter, except for oil series 2A. Oil series 2A differs from the other test runs in that the engine operating conditions during this test was abnormal. This oil series 2A was carried out at an engine load of 1.46 kW, which is over 20 percent above the designed maximum rated peak power for the Petter AA1. This suggests that the increase in oxidation levels is due, in part, to an increase in acidity. The slope of the graph was found to be 0.25 (mg KOH/g/oxygen content). The degree of change of TAN with oxidation level increase is small and indicates that the amount of acidity derived from oxidation is due to a correspondingly small amount of (weak) organic acids present in the used oil. This is likely in that (strong) inorganic acids would have been neutralised by the TBN constituents and that most of the acidic gases have been removed with the exhaust gases.

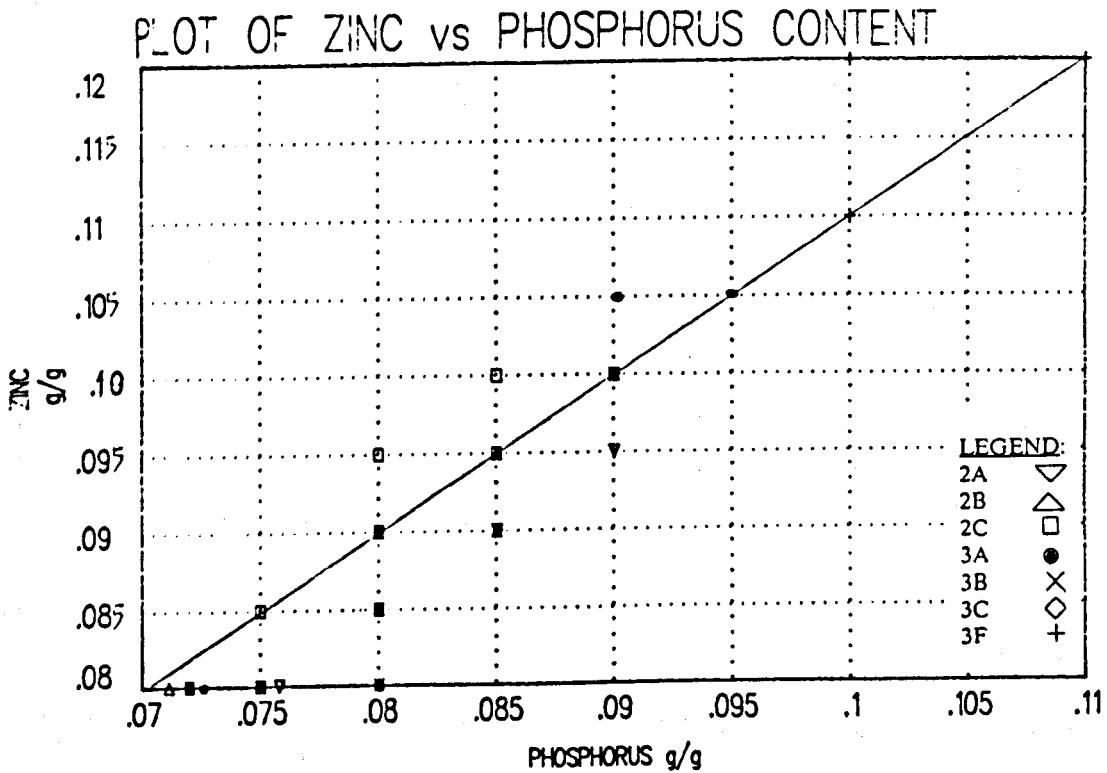
**FIGURE 71: PLOT OF PERCENTAGE TOTAL INSOLUBLE MATTER AGAINST OIL MAKE-UP MASS.**



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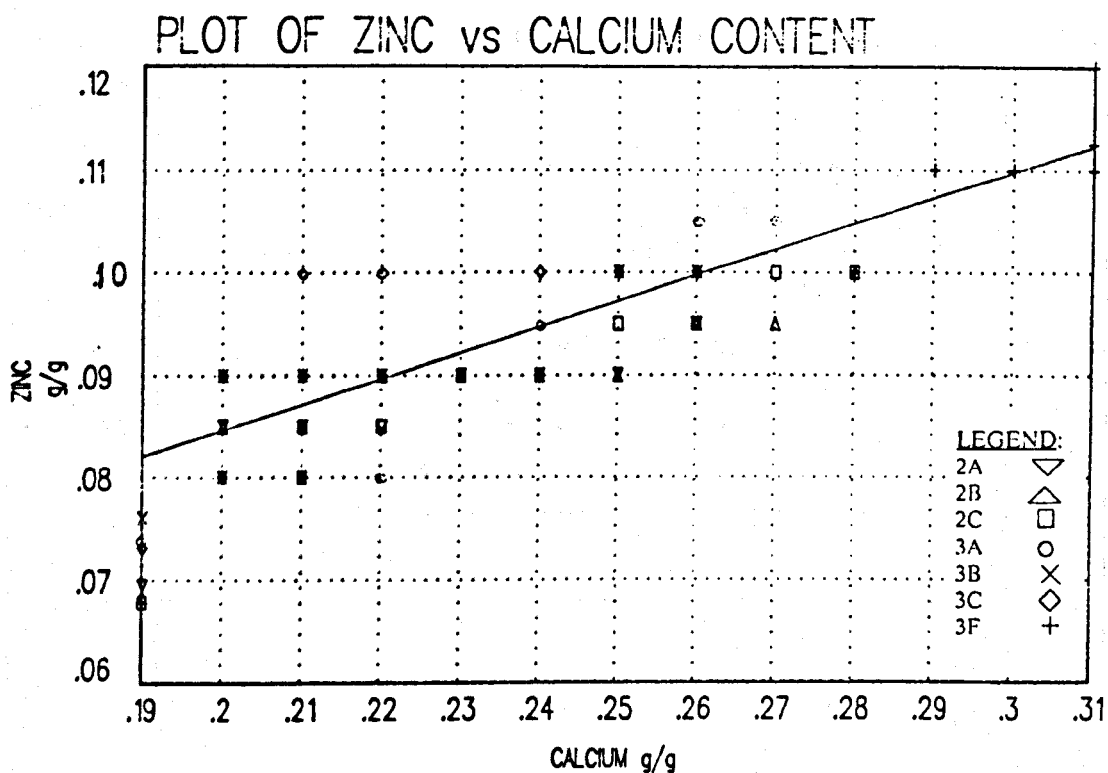
**FIGURE 72: PLOT OF ZINC AGAINST PHOSPHORUS CONTENT.**



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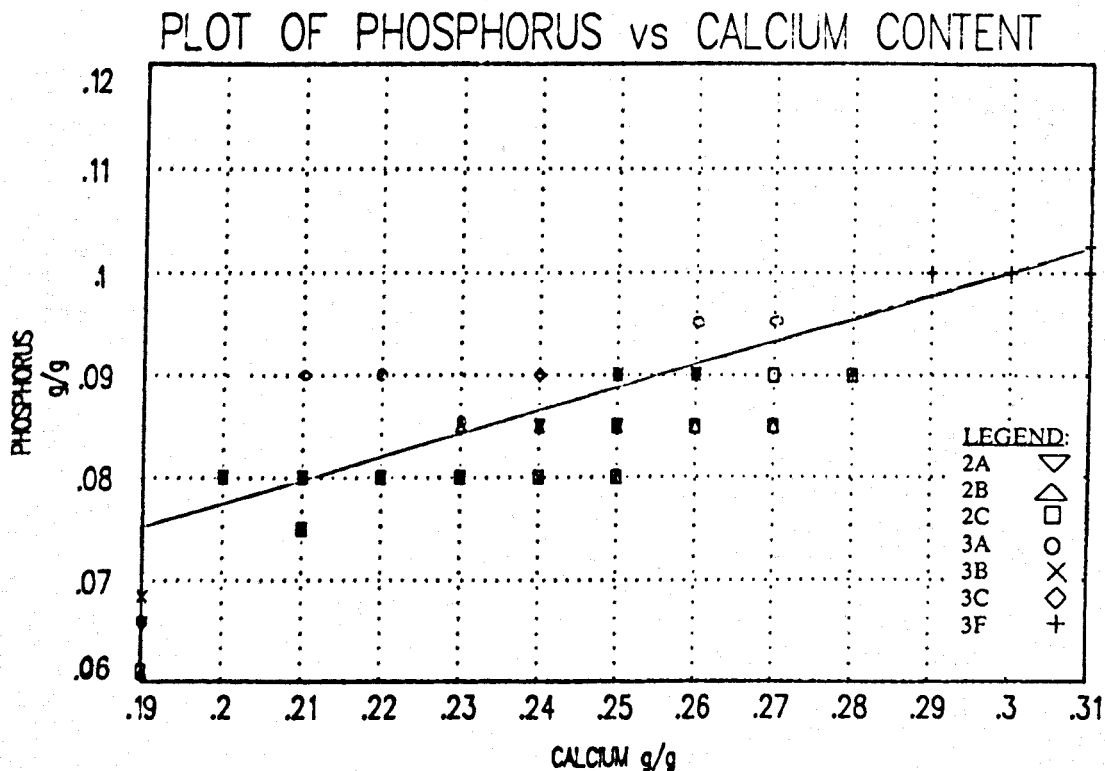
FIGURE 73: PLOT OF ZINC AGAINST CALCIUM CONTENT.



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FIGURE 74: PLOT OF PHOSPHORUS AGAINST CALCIUM CONTENT.

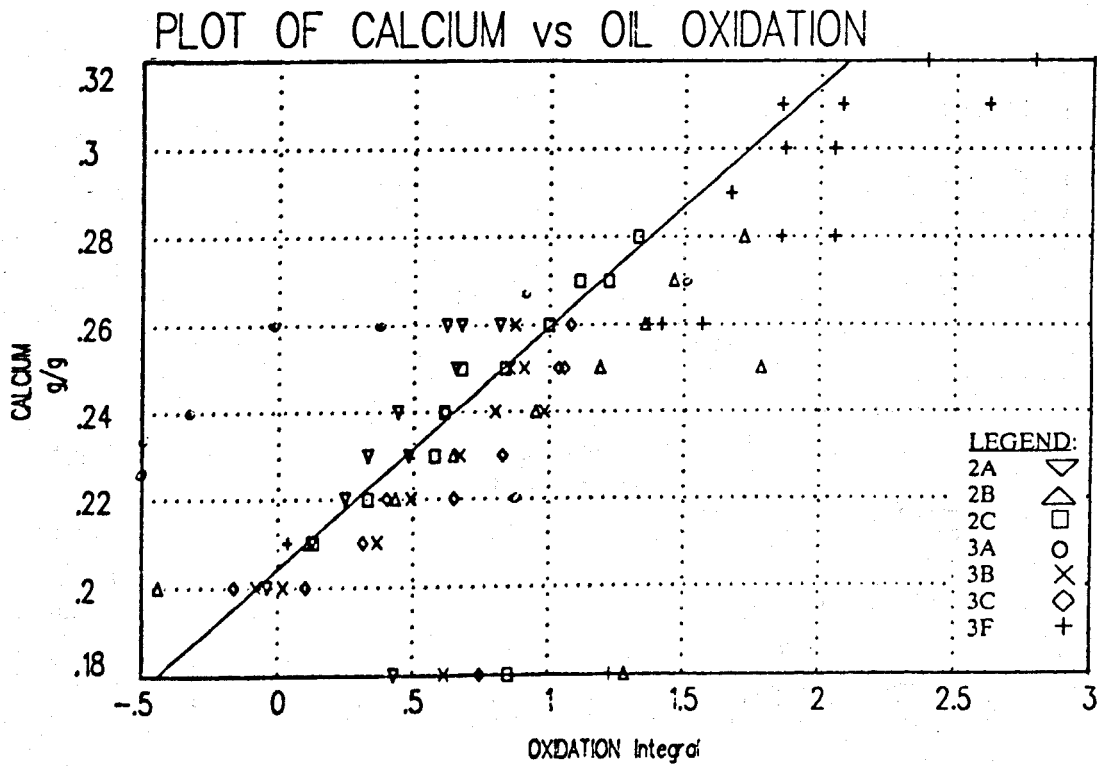


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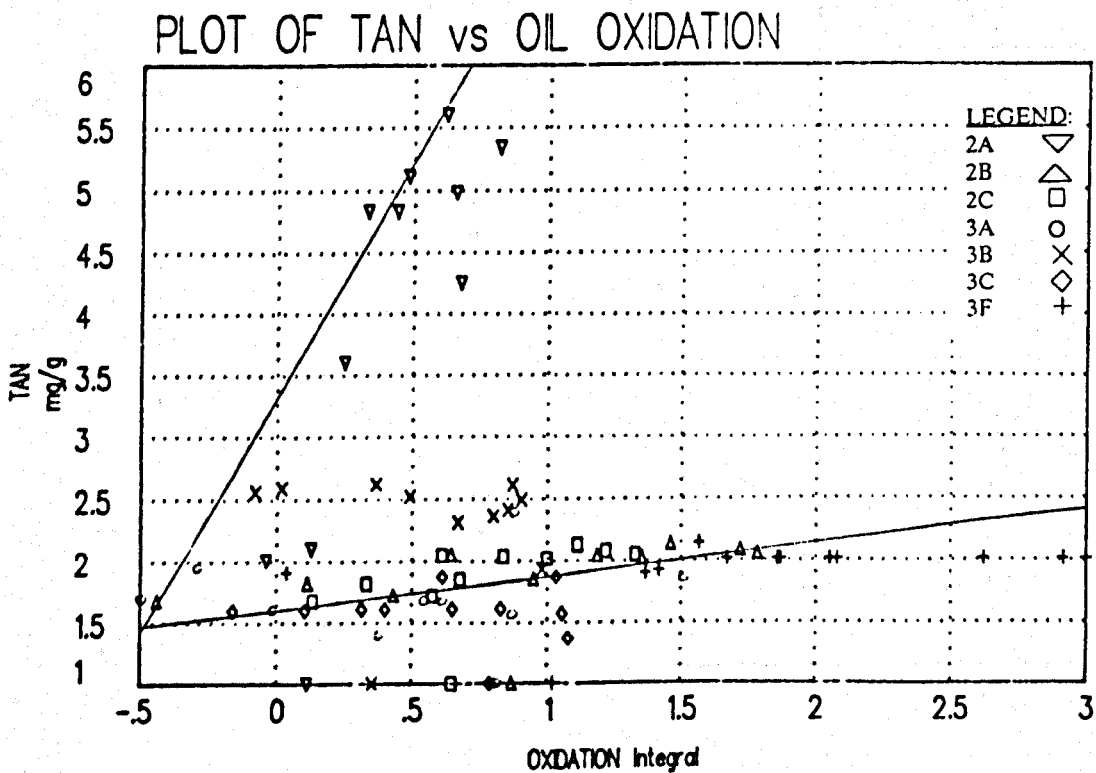
FIGURE 75: PLOT OF CALCIUM CONTENT AGAINST OIL OXIDATION.



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FIGURE 76: PLOT OF TOTAL ACID NUMBER AGAINST OIL OXIDATION.

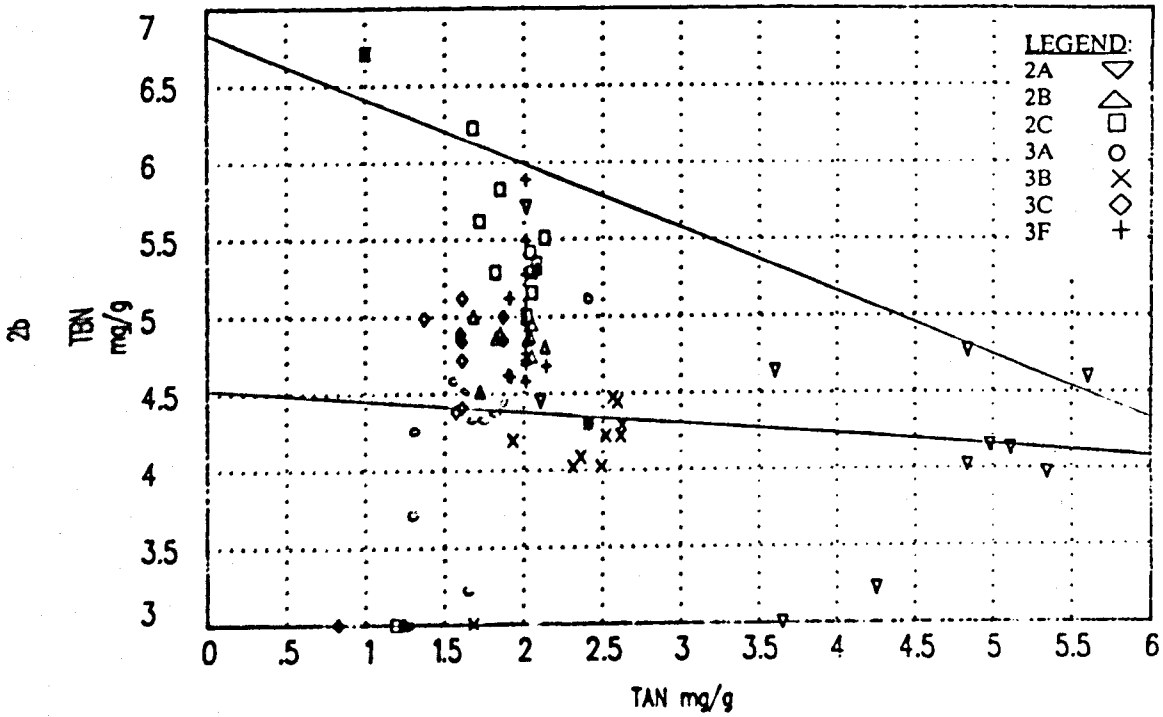


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FIGURE 77: PLOT OF TOTAL BASE NUMBER AGAINST TOTAL ACID NUMBER.

PLOT OF TBN vs TAN

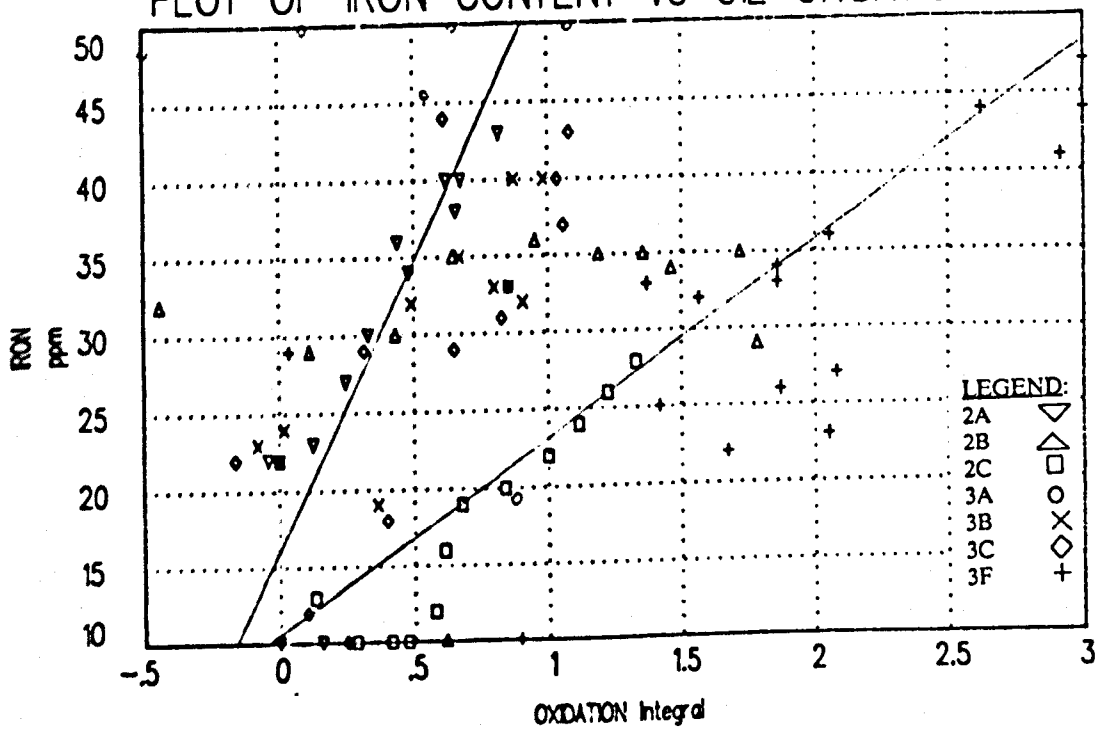


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FIGURE 78: PLOT OF IRON CONTENT AGAINST OIL OXIDATION.

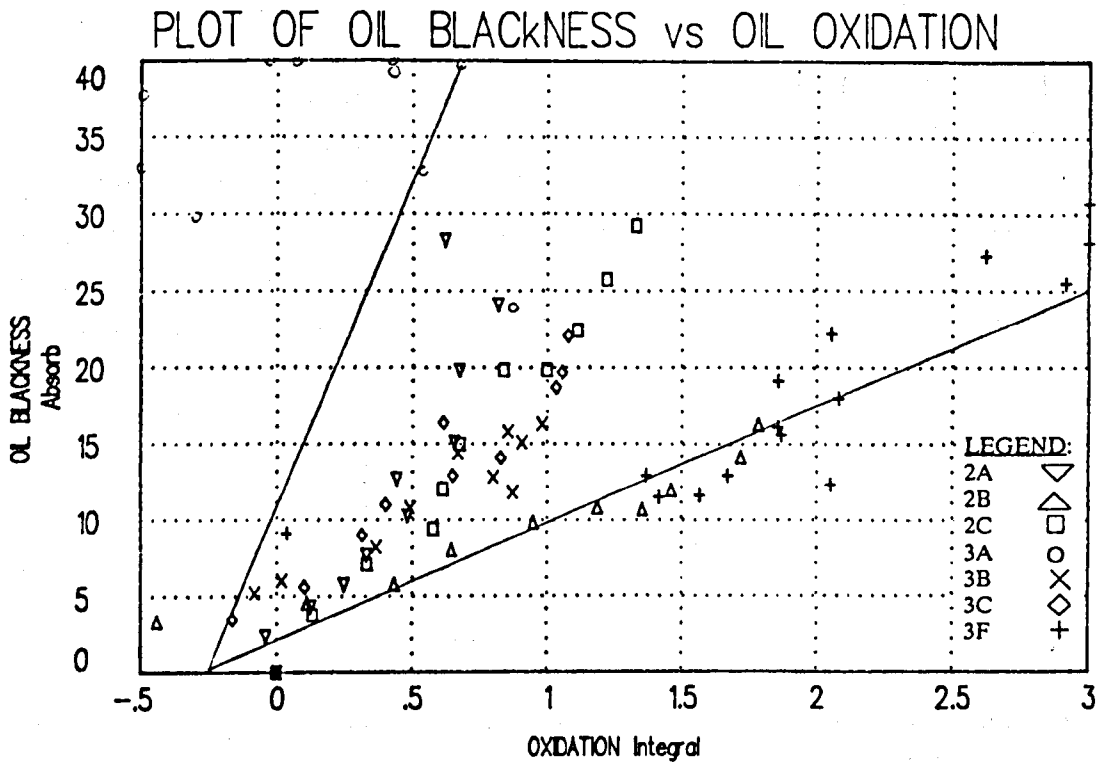
PLOT OF IRON CONTENT vs OIL OXIDATION



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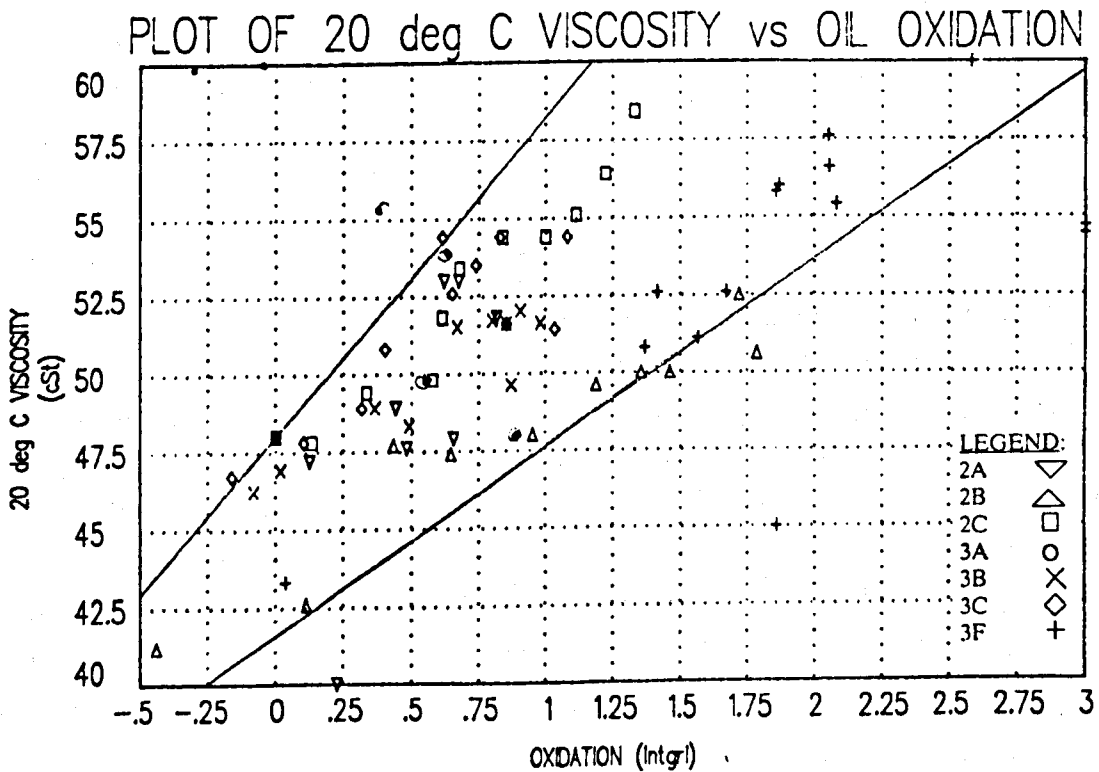
FIGURE 79: PLOT OF OIL BLACKNESS LEVEL AGAINST OXIDATION.



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FIGURE 80: PLOT OF OIL VISCOSITY AT 20 °C AGAINST OIL OXIDATION.



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#### 4.9.9.5 Total Base Number versus Total Acid Number.

The plot of Total Base Number against Total Acid Number gives a negative gradient of 0.5, Figure 77. This indicates that the TAN value increases at twice the rate at which the TBN value decreases. The graph indicates that the TAN value will be equal to the TBN value of 4.5 mg KOH/g. When this condition is passed, then it may be considered that the oil's safe alkaline reserve threshold (limit) has been exceeded and accelerated wear rates may result. Retrospective analysis of the data (Figures 65(a) and 65(d)) show that when the TBN values fall below the 4.5 mg KOH/g level, the TAN values do not change significantly but the oil consumption rises above previous levels recorded for that test series. The continued trends of these results suggest that the loss of oil consumption control would follow soon after the TBN having fallen below the 4.5 mg KOH/g level. This data suggests that the engine loses oil consumption control as a result of corrosive wear which also causes severe bore polishing.

#### 4.9.9.6 Iron Content versus Oxidation.

The plot of iron content against oxidation level was made to see whether or not the wear rate was being accelerated by increasing levels of oxidation of the oil, Figure 78. The cross-plot of iron against oxidation does indicate a certain degree of catalysis of the oxidation products on the wear of the cylinder bore. The results are scattered and no generalisation can be made on the rates or minimum oxidation level because of this. The accelerated wear cannot, however, be credited solely to the oxidation of the oil, as the acidity imparted by the high sulphur diesel fuel to the combustion gases would be the more likely candidate (for the corrosive wear). What is possible in the bulk of the used oil, is that the iron is kept in suspension by the oxidised oil, similar in manner to that for the calcium mentioned above.

#### 4.9.9.7 Oil Blackness versus Oxidation.

There is an initially linear relationship between the degree of Oil Blackness and Oxidation, which depends on the oil consumption and engine load (engine E2 being abnormally, high loaded during test 2A), Figure 79. For the high engine loads, the blackness increases rapidly with the oxidation of the oil. For an engine accompanied by high oil consumption, the blackness increase is lowered by the diluting effect of oil make-up levels. For an engine under normal operating conditions, the blackness increases linearly with the oxidation of the oil, at a rate of about 20 (Absorbance/Oxidation). This suggests that the oil becomes progressively oxidised and contaminated with soot and wear debris which are selectively accumulated in the

oil.

#### 4.9.9.8 20 °C Viscosity versus Oxidation.

The plot of the viscosity at 20 °C against oxidation shows a linear relationship. Test 2A again displays a higher level of degradation than the other tests. The other tests differ from 2A with the slope of the graph being 4 (cSt/Oxidation), Figure 80. This relationship suggests that the increase in viscosity is a result of the oxidation of the oil in addition to the fragmentation of the viscosity index improver polymers discussed previously. The oxidation products must be forming high molecular mass cross-linked networks to a greater extent than at first thought. It is, therefore, possible that the smaller VII fragments only make a minor contribution to the low temperature viscosity on their own, but once they become cross-linked with oil oxidation products, then they increase the viscosity of the oil significantly.

#### 4.10 SUMMARY OF OIL ANALYSIS.

The TBN and 100 °C viscosity decline with time. The TAN and TBN trends compliment one another but stabilise to a constant value after 40 hours. The TBN values stabilise to about 4.5 mg KOH/g and the TAN values stabilise at about 2.0 mg KOH/g. The rapid initial decline of TBN suggests the presence of both fast reacting, inorganic TBN constituents and the presence of slow reacting, organic TBN constituents. The trends suggest that the organic TBN constituents are removed non-selectively, along with the combustion of the base oil.

The oil viscosities at 20 °C and 40 °C have a rising trend with the aging of the oil, along with calcium, oxidation, metals, and oil blackness. This trend indicates that these parameters are accumulating due to selective removal of light oil fractions.

The Total Insoluble Matter is related, proportionally, to the mass of oil make-up. These two parameters are directly related due to the dilution effect of high oil make-up, which in turn, is due to high oil consumption. The trends indicate non-selective removal of these components.

Zinc and phosphorus levels are proportionally related to one another (stoichiometrically) and have a different removal mechanism from all the other parameters. These elements are being selectively accumulated at an apparently lower rate than that for the other elements.

## CHAPTER 5.

### 5. ENGINE WEAR AND OIL DEGRADATION MODELS - AN INTRODUCTION.

An internal combustion engine and the lubricating oil within it should be considered as two interacting sub-systems of a single, dynamic system. The behaviour of the engine and oil system is described quantitatively by the intrinsic interacting parameters related to both the engine's mechanical wear and the oil's chemical degradation. This chapter, therefore, describes a model where the engine's mechanical wear rate and lubricating oil degradation rates are considered simultaneously. The only other similar approach to this problem has been that of Dyson [33].

The first approach considers the engine lubricating oil degradation model, section 5.1 below.

#### 5.1 LUBRICATING OIL DEGRADATION MODEL.

An engine can be described in terms of a flow (dynamic) stirred tank reactor as well as a static, closed tank reactor. The flow characteristics arise from the use of lubricating oil and its makeup level simultaneous to fuel consumption. Whilst this is a well known concept in chemical technology, it has not been previously applied to the degradation of lubricating oil in an internal combustion engine.

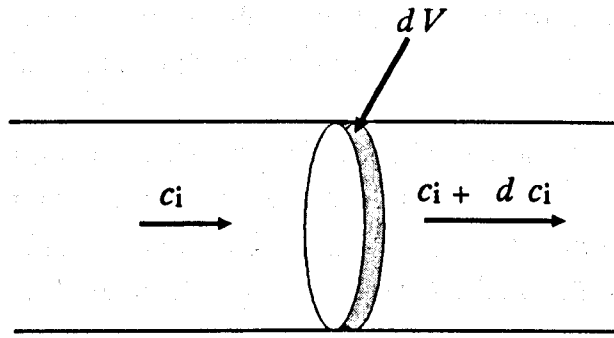
Consider a simple, tubular, flow reactor (Figure 81) in which the volume,  $u$ , of reactants enter continuously at the inlet of the reaction vessel and the product mixture of the same volume,  $u$ , is withdrawn at the outlet. Consider a particular component,  $k$ , in a volume element,  $dV$ , sliced out of the tube whose inlet concentration is,  $c_k$ , and its outlet concentration is,  $c_k + dc_k$ . If there is no longitudinal mixing, the net change with time of the number of moles of,  $k$ , within,  $dV$ , ( $dn_k/dt$ ) is the sum of two terms, namely, one due to chemical reaction within,  $dV$ , and the other equal to the excess of,  $k$ , entering over that leaving. Thus,

$$\frac{dn_k}{dt} = r_k dV - u d c_k \quad \text{Eqn. 25}$$

The chemical reaction rate per unit volume is denoted by,  $r_k$ . The explicit form of,  $r_k$ , is determined by the rate law for the reaction: for a zero order reaction, with respect to,  $k$ ,  $r_k = k_0$ , for a first order reaction,  $r_k = -k_1 c_k$ ; for a second order

reaction,  $r_k = -k_2 c_k^2$ .

FIGURE 81. A SIMPLE TUBULAR FLOW-REACTOR.



After reaction in the flow system has attained a steady state, in which the number of moles of each component in any volume element no longer changes with time, the net flow into the element then exactly balancing the reaction within it, and then  $dn_k/dt = 0$ , and Equation 25 becomes:

$$r_k dV - u d c_k = 0 \quad \text{Eqn. 26}$$

If,  $r_k$ , is introduced as a function of,  $c_k$ , the equation (26) can be integrated, for example, with  $r_k = -k_1 c_k$ ,

$$- k_1 \frac{dV}{u} = \frac{d c_k}{c_k} \quad \text{Eqn. 27}$$

When integration is carried out between the inlet and the outlet of the reactor it gives Eqn 29:

$$\frac{-k_1}{u} \int_0^{V_0} dV = \int_{c_{k_1}}^{c_{k_2}} \frac{d c_k}{c_k} \quad \text{Eqn. 28}$$

$$- k_1 \frac{V_0}{u} = \ln \frac{c_{k_2}}{c_{k_1}} \quad \text{Eqn. 29}$$

The total volume of the reactor is  $V_0$ , and  $c_{k_1}$  and  $c_{k_2}$  are the concentrations of  $k$  at the outlet and inlet of the tube, respectively.

It may be noted that Eqn. (29) reduces to the integrated rate law for a first order reaction in a static system if the time,  $t$ , is substituted for  $(V_0/u)$ , where  $(V_0/u)$  is defined as the contact time for the reaction; this is the average time that a molecule would take to pass through the reactor. Thus Eqn. (29) allows the rate constant  $k_1$ , to be calculated from a knowledge of the contact time and of the reactant concentrations at the inlet and the outlet of the reactor.

The fundamental approach of the above kinetic derivation of a flow reactor needs to be extended further, to incorporate the stirred nature of engine oil degradation. The derivation of Eqn (26) tacitly assumed that there was no volume change,  $dV$ , as a result of the reaction. A volume change would affect the flow rate at constant pressure, particularly for gaseous flow reactions, but for liquid flow systems the effects of change in volume are generally negligible.

But in a stirred flow reactor in which the inlet flow is exactly equal to that of the outlet flow, the composition of the mixture in the reactor is unchanged when a steady state is achieved. Eqn. (26) still applies, but in this case  $dV = V_0$  the total reactor volume, and  $d c_k = c_{k_1} - c_{k_2}$  where  $c_{k_1}$  and  $c_{k_2}$  are the initial and final concentrations of the component,  $k$ . Thus,

$$r_k = \frac{u}{V_0} (c_{k_2} - c_{k_1}) = \frac{d c_k}{dt} \quad \text{Eqn. 30}$$

With this method, there is no need to integrate the rate equation. One point on the rate curve is obtained from each steady-state measurement of a number of tests with different feed rates and initial concentrations is required to determine the order of the reaction. Applying this approach to an engine lubrication system, if the engine oil level in the sump is kept quasi-constant by periodic topping-up, then the above kinetic derivation can be applied to the study of engine oil degradation. Due to the continuous loss of oil and its degradation compared to the periodic nature of oil volume top-up, the total engine and oil system is best described as a Quasi-Continuous Stirred Tank Reactor (QCSTR). A single engine lubricant degradation system is a simplification. Two areas of lubricant degradation are the sump and the combustion chamber/piston/bore region. This engine reactor model comprises of two interacting mixing chambers (Maeda, Maeda and Yasutomi, [17], namely:

1. Engine "top-end" - an intensive (high temperature and pressure) and highly reactive, small volume, stirred, flow reactor, and



2. Engine sump - a relatively benign (low temperature and pressure), large volume reactor which is vigorously stirred by the rotating (dipping) crankshaft, gears and oil pump.

The lubricating oil within the engine sump of volume,  $V_s$ , is periodically topped up with fresh oil volume,  $V_f$ , of the same composition as that in that originally present in the sump. Part of the sump oil that is pumped to the "top-end" of the engine is lost,  $V_i$ , through leaks, combustion and selective evaporation of volatile oil constituents, before the remaining oil and part of the reacted oil is returned to the sump. The volumes and reaction rates between the two reactors are the subject of a separate, higher degree thesis by S.D. Cupples at Leicester Polytechnic. This thesis is concerned with a single reactor approach centred on the engine sump only.

The concentration of an oil additive or degradation product,  $X$ , can be described by the mass balance equation (30), containing zero and first order rate constants,  $k_0$  and  $k_1$ , respectively:

$$dX/dt = -k_1 + k_0 \quad \text{Eqn. 31}$$

where:

$$k_1 = k_f + k_s + k_v \quad \text{Eqn. 32}$$

$$k_0 - k_{add} X_0 = (k_f + k_s + k_v) X_0 \quad \text{Eqn. 33}$$

where:

$k_f$  = rate constant for oil leaks from the engine

$k_s$  = rate constant for oil sampling

$k_v$  = rate constant for oil volatilisation

$k_{add}$  = rate constant for oil (fresh) addition

Integration of Eqn. 31 gives:

$$X = X_a - (X_a - X_0) \exp(-k_1 t) \quad \text{Eqn. 34}$$

where:

$$X_a = k_{add} X_0 / k_1 \quad \text{Eqn. 35}$$

$X_a$  = equilibrium concentration

$X_0$  = initial concentration

From Eqn. 35,  $k_{add}$  can also be represented by  $k_{add} = k_1 X_a / X_0$

The value of  $k_{add}$  can be calculated from those of  $k_1$ ,  $X_a$  and  $X_0$  which are determined by the analysis according to Eqn. 34. The mass rate of oil addition,  $R_{add}$  can be obtained from the Eqn. 36, by knowing the quantity of engine (sump) oil charge,  $Q$ .

$$R_{add} = k_{add} Q \quad \text{Eqn. 36}$$

Consider the depletion of Total Base Number of the oil:

$$d C_{TBN} = C_{TBN_1} - C_{TBN_2} \quad \text{Eqn. 37}$$

where  $C_{TBN_1}$  and  $C_{TBN_2}$  are the initial and final TBN values, respectively.

From the original exposition by Denbigh [19] concerning the kinetics of stirred tank reactors, where the overall inlet oil flow is equal to the overall outlet oil flow, it follows that the steady-state concentration is given by Eqn. 38:

$$- \frac{d_{TBN}}{dt} = (C_{TBN_1} - C_{TBN_2}) \frac{U}{V} = r_{TBN} \quad \text{Eqn. 38}$$

An example calculation based on Table 38 (Series 3B, 80 and 90 hours data, column 2 from the left):-

$$- d_{TBN} = (4.19 - 4.02) \times 154/1402 = r_{TBN}$$

$$r_{TBN} = 0.17 \times 154/1402$$

$$r_{TBN} = 0.019 \text{ mg KOH/g/10 Hours}$$

$$r_{TBN} = 0.002 \text{ mg KOH/g/Hr}$$

The high rate of oil consumption and its subsequent replenishment is probably the most important factor preventing any significant depletion of TBN. The other main contributory factors include the level of sulphur within the fuel, the fuel flow rate and the rate of flow of blowby gases, which in turn reflects the mechanical wear rate of the engine.

Table 42 summarises the 10 hourly rate data averaged over each of the test runs for series 2A - 3C. Table 43 summarises the averaged rate data (per hour) for each of the test series over each 100 hour test. Note that the averages of the averaged data in the two tables, calculated by the two different methods give similar rate values. The first

(fresh oil) data points were not included in the calculation of the averages.

## 5.2 COMPARISON WITH OTHER OIL DEGRADATION MODELS.

A different approach, namely, that of Dyson, *et al*, [33] proposed a mathematical model predicting the TBN depletion rate from the amount of fuel sulphur:

$$TBN_t = TBN_0 - A (1 - e^{-rt}) \quad \text{Eqn. 39}$$

where:  $A = 0.35 YFS$  = Neutralising effect,  
and:

$Y$  = Conversion ratio,  
 $F$  = Ratio of fuel to oil consumption,  
 $S$  = Percentage of sulphur in the fuel,  
 $r$  = Ratio of oil consumption to oil charge,  
 $t$  = Time (duration) of test

The Dyson derivation assumes that the oil consumption and replenishment rates are equal and is continuous. Testing this model with the field data obtained, the following is found:

$$\begin{aligned} TBN_t &= TBN_0 - A (1 - e^{-rt}) \\ TBN_0 - TBN_t &= A (1 - e^{-rt}) \\ TBN_0 - TBN_t &= 0.35 YFS (1 - e^{-rt}) \\ Y &= \frac{TBN_0 - TBN_t}{0.35 FS (1 - e^{-rt})} \end{aligned} \quad \text{Eqn. 40}$$

An example calculation based on the averaged 10 hour data, see Table 41, for the 10 Oil Hours data, TBN and Oil Consumption data:-

Average fuel consumption = 680 g per hour  
Average oil consumption = 26.1 g per hour  
Average (sump) oil charge = 1500 g  
Fuel sulphur content = 1%  
New oil TBN (TBNO) = 6.71 mg KOH/g by IP 177)  
Used oil TBN (TBNt) = 5.23 mg KOH/g

Substituting these values in the Eqn. 40 above:

$$Y = \frac{\text{TBN}_0 - \text{TBN}_t}{0.35 F S (1 - e^{-rt})}$$

$$Y = \frac{6.71 - 5.23}{0.35 \times (26.1/680) \times 1 \times (1 - e^{-(261/1500)})}$$

$$Y = 0.20\%$$

The value obtained for  $Y$ , the conversion ratio, lies within the range of values obtained by Sharma [34] and Dyson [33]. These workers obtained values of  $Y$ , typically in the range 0.15 to 0.4%. The value of 0.20% for  $Y$  obtained from the work carried out at Leicester lies in the middle of the range obtained by Sharma and Dyson. This indicates that the test engine is behaving in a manner consistent with other engines as regard to oil consumption, blowby and fuel dilution.

A second comparison could be done directly by calculating the theoretical amount of sulphuric acid that can be obtained from the conversion of fuel sulphur. The sulphuric acid produced can then be used to calculate the amount of TBN depleted, assuming all the sulphuric acid reacts with the TBN additives. The sulphur throughput for the engine is in the region of 6.8 g per hour. The amount of sulphur entering the oil was determined for two, ten hour used oils, and a new oil sample. The new oil was found to contain 1.07% sulphur and the average sulphur content of the two 10 hour used oils was found to be 1.14%. The sulphur content was determined by a x-ray spectroscopic technique known as X-ray Fluorescence Spectroscopy (XFS). This technique revealed that about 15% of the sulphur disappeared during the measurements. This indicates that the sulphur must have been trapped as a non-reactive gaseous product which was released during the measurements. Ignoring this loss of gaseous sulphur, the amount of sulphur entering the oil through blowby can, conservatively, be calculated to be (a rate of) 0.007% per hour. This data can be used to calculate the TBN depletion time assuming that only sulphur (as sulphuric acid) neutralises the TBN.

$$\text{Total TBN} = 6.71 \times 1500 \quad \text{Eqn. 41}$$

$$= 10.06 \text{ g KOH}$$

$$= 10.06/56.1$$

$$= 0.179 \text{ mol KOH}$$

$$\text{Sulphur addition} = 0.007/100 \times 1500 \quad \text{Eqn. 42}$$

$$= 0.105 \text{ g/hour}$$

$$= 0.0033 \text{ mol/hour}$$

The time to completely neutralise KOH, assuming two moles of KOH reacts with one mole of H<sub>2</sub>SO<sub>4</sub>, is as follows:

$$\begin{aligned} \text{Time (TBN} \rightarrow 0) &= 0.179 / (2 \times 0.0033) && \text{Eqn. 43} \\ &= 27 \text{ hours} \end{aligned}$$

The TBN level does not decrease to zero in the time calculated above, due to oil replenishment and also due to all the sulphur entering the engine not being converted to sulphuric acid in the lubricant. The presence of acids other than sulphuric acid in the used oil, however, should in theory, reduce this TBN neutralisation time even further. The TBN neutralisation time of 27 hours obtained suggests that only part of the sulphur entering the engine is converted to sulphuric acid of which some fraction enters the lubricating oil and then neutralises the TBN.

The modelling of TBN depletion has been shown to be meaningless when considered on its own. The TBN value must be considered together with the associated TAN values and other oil/engine parameters when using it as a measure of oil life/quality. This is because the TBN and TAN values are the result of reactions occurring over a wide kinetic (reactivity) range. The modelling of wear metals, soot, oxidation and viscosity changes during the life of the oil follow simple zero order kinetics. The behaviour of these parameters follows the Quasi-Continuous Stirred Tank Reactor (QCSTR) model.

### 5.3 THE GENERAL QUASI-CONTINUOUS STIRRED TANK REACTOR (OCSTR) MODEL.

The changes in mass or concentration of any property of the used oil can be followed by the integrated form of the complete system material balance described below. Consider the stirred tank reactor as depicted in Figure 82, for any component level in the system:

$$\text{Initial} + \text{Total Make-up} = \text{Final} + \text{Loss from System} + \text{Loss by chemical change}$$

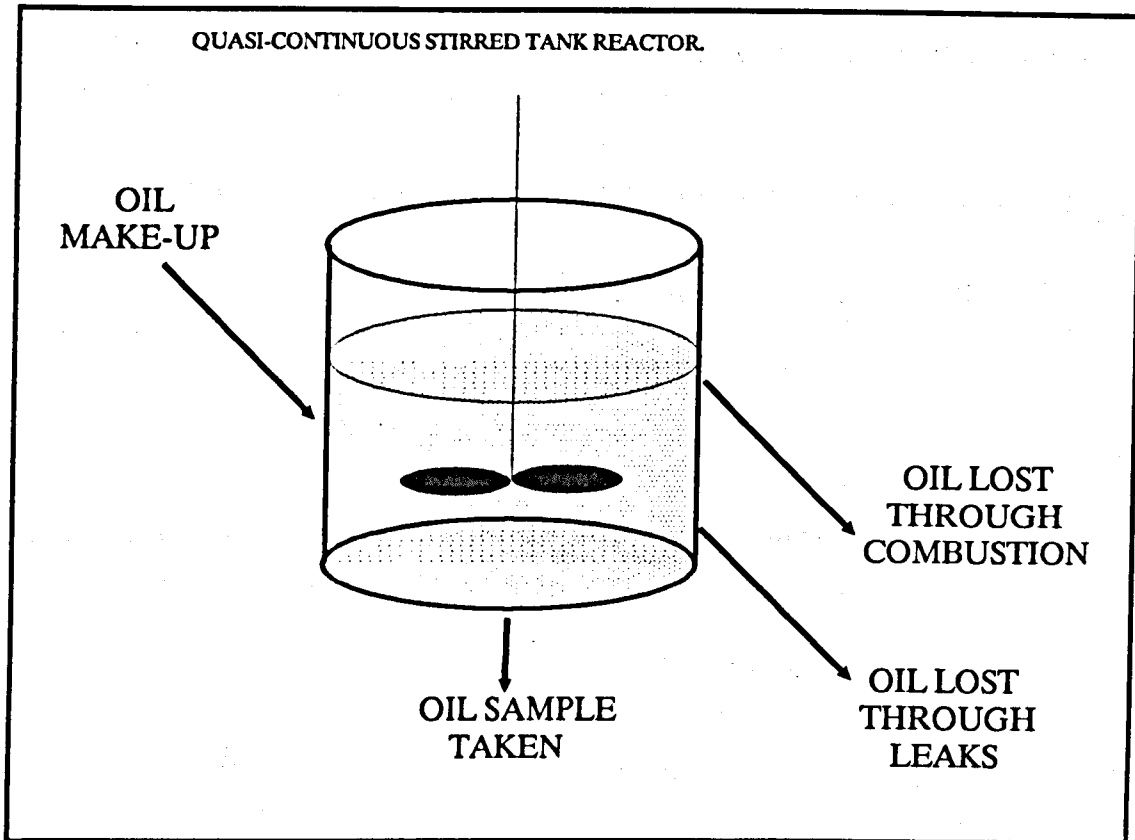
$$\text{For the oil:} \qquad \qquad \qquad \text{Eqn. 44}$$

$$\text{Initial} + A_1 + A_2 + \dots = \text{Final} + L_1 + L_2 + \dots + C_1 + C_2 + \dots \qquad \text{Eqn. 45}$$

where:

Initial is the original mass of component  
 Final is the component mass at the end,  
 $A_x$  is the mass of make-up,  
 $L_x$  is the mass of Oil consumed (Total Loss), and  
 $C_x$  is the mass of component lost by chemical change.

FIGURE 82. GENERAL OIL DEGRADATION MODEL BASED ON QCSTR.



For an oil component or property, say TBN:

$$\begin{aligned}
 \text{TBN}_0 (\text{Initial} + A_1 + A_2 + \dots) = M_f \text{TBN}_f + L_1 \cdot \text{TBN}_1 + L_2 \cdot \text{TBN}_2 + \dots \\
 + k (\text{TBN}_1 t_1 + \text{TBN}_2 t_2 + \dots) \quad \text{Eqn. 46}
 \end{aligned}$$

where  $C_x = M_f k t$  (that is, the product of time,  $t$ , and the rate of degradation,  $k$ ), and  
 $M_f$  = Final oil mass in sump.

Using the data from the averaged data in Table 41, for the 10 Oil Hour TBN data:

$$6.71(1500 + 2347) = (1535 \times 4.73) + 11534 + (k \times 664 \times 2457)$$

$$25813 = 7250 + 11534 + 1631448.k$$

$$k = 0.043 \text{ mg KOH/g/hr}$$

The value of  $k$  obtained above, the rate of TBN degradation per hour, is the true or actual rate of degradation of TBN. The values obtained in Table 43 is the observed rate of TBN degradation. The rate of change of any component in the system can be obtained by a similar treatment which gives:

$$\text{Rate}_{\text{Accumulation}} = \text{Rate}_{\text{Supply}} - \text{Rate}_{\text{Removal}} + \text{Rate}_{\text{Formation}} \quad \text{Eqn. 47}$$

From this it can be seen that for a steady state condition where there is no net accumulation:

$$\text{Rate}_{\text{Supply}} = \text{Rate}_{\text{Removal}} \quad \text{Eqn. 48}$$

Consider the Oil in the system in which the purpose of the oil top-up procedure is to maintain a constant mass in the system:

$$\text{Rate}_{\text{Accumulation}} = 0 \quad \text{and so,}$$

$$\text{Rate}_{\text{Supply}} = \text{Rate}_{\text{Removal}} (\text{Combustion} + \text{Leaks} + \text{Sample}) \quad \text{Eqn. 49}$$

$$\frac{dA}{dt} = \frac{dL}{dt} \quad \text{Eqn. 50}$$

For a component or property, say TBN

$$\frac{d(M.TBN_c)}{dt} = \frac{d(A.TBN_o)}{dt} - \frac{d(L.TBN_s)}{dt} + \frac{d(C.TBN_c)}{dt} \quad \text{Eqn. 51}$$

where  $M$  is the system oil mass at any time,  $t$ ,

$A$  is the mass of Make-up oil,

$L$  is the mass of component lost through oil consumed,

$C$  is the mass of component degraded/produced chemically,

$TBN_0$  is the Initial TBN (Fresh Oil),

$TBN_s$  is the TBN of the used oil at time,  $t$ , and

$TBN_c$  is the average TBN lost by degradation.

Substituting the averaged TBN, Oil Make-up and Oil Consumption data from Table 41, last line :

$$\frac{1376 \times 4.67}{10} = \frac{235 \times 6.71}{10} - \frac{246 \times 4.67}{10} - k \cdot \text{TBN}_c$$

$$642.6 = 157.7 - 114.9 - k(6.71 - 4.67)$$

$$-2.04 k = 599.8$$

$$k = -294 \text{ mg/hr}$$

This value can be checked by noting that  $C = k \cdot t$

The convention used for  $k$  is that  $k$  is negative for a component or property that decreases with time and positive for one that increases with time.

An example calculation based on the averaged 10 hour data, see Table 41, first and last lines for TBN and Sump Mass data, the average mass of TBN depleted per hour starting with new oil is:

$$\begin{aligned} k &= \frac{C \times \text{TBN}_c}{t} && \text{Eqn. 52} \\ &= 1376 \times 2.04 / 10 \\ &= 280 \text{ mg/hr} \end{aligned}$$

The rest of the data obtained can be treated in a manner similar to that demonstrated for the oil and TBN shown above. A simpler treatment can be obtained when the sump mass remains constant, in which case the above equations can be simplified to:

Consider an oil parameter  $X$ ,

$$\text{Net (Apparent) Change} = \text{Added} - \text{Loss (Actual)} \quad \text{Eqn. 53}$$

$$\frac{dX \times M}{dt} = \frac{dX \times A}{dt} - \frac{dX \times L}{dt} \quad \text{Eqn. 54}$$

For the case where there is no contribution of a parameter due its absence in the fresh oil, the above equation is then reduced to the apparent change being the actual change in its level. This would be the case for Total Insoluble Matter, Wear Metals and Oxidation parameters.



The Quasi-Continuous Stirred Tank Reactor model shown by the above calculations yields a closer representation of the degradation of the oil and its degradation parameters in real operating engines. This model can be used for a wide range of engines and operating conditions, as it includes both oil consumption and oil make-up effects. Simpler models assume that the oil lost and make-up are equal or that they are close to zero. This model, therefore, be used to model lubricating oil degradation of long, extended test runs covering the life of an engine. The above mentioned model can be improved by firstly obtaining oil analysis data continuously from on-line measurements, and secondly, by determining the interaction between the small but intense reactor, the top-ring zone, and the relatively benign large reactor, the sump.

#### **5.4 SUMMARY OF CHAPTER 5.**

Two different models that had been proposed previously for the rate of TBN depletion have been verified. The Quasi-Continuous Stirred Tank Reactor (QCSTR) model has been shown to be a more extensive and representative model of lubricating oil degradation in the engine system under investigation than the model of Dyson, previously considered.

The Quasi-Continuous Stirred Tank Reactor Model takes into account the effect of both oil consumption and oil make-up, which is more representative of real operating engines. The lubricating oil degradation under real operating conditions can, therefore, be modelled more realistically for extended test runs over the life of an engine.

TABLE 41: AVERAGED 10 HOUR DATA FOR TEST SERIES 2A, 2B, 2C, 3A, 3B, 3C, 3F.

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	6.71	1.00	48.0	19.2	4.20	0.21	0.08	0.08	20	2	1	3	2	5	4	0.0	0.0	0	1500	0.00	0.00
10	5.23	1.99	44.0	18.2	3.53	0.21	0.08	0.08	22	5	1	4	6	7	7	7.0	19.9	0	1499	0.00	0.05
20	4.73	1.94	47.3	19.9	3.60	0.21	0.09	0.08	24	6	2	5	3	8	5	10.1	14.7	310	1505	1.74	0.21
30	4.68	2.16	48.0	20.4	3.70	0.22	0.09	0.08	28	7	2	5	3	8	4	13.0	16.8	202	1475	1.13	0.43
40	4.50	2.47	49.7	19.8	3.58	0.23	0.09	0.08	30	8	2	5	3	9	4	14.4	15.3	262	1486	1.46	0.17
50	4.69	2.40	53.0	20.4	3.58	0.24	0.09	0.08	35	10	3	6	4	8	5	16.5	15.7	245	1482	1.37	0.45
60	4.79	2.47	53.1	20.9	3.97	0.24	0.09	0.08	35	10	3	6	3	9	4	16.7	15.9	252	1502	1.41	0.63
70	4.37	2.47	53.5	20.6	3.42	0.25	0.10	0.09	39	11	3	7	4	9	5	19.4	15.4	272	1514	1.52	0.71
80	4.39	2.27	52.8	20.7	4.10	0.26	0.10	0.09	41	13	3	7	3	9	5	21.5	17.2	225	1490	1.26	0.94
90	4.60	2.52	55.1	21.5	3.82	0.26	0.10	0.09	40	25	4	7	6	9	7	25.6	16.1	284	1497	1.61	1.99
100	4.73	2.56	54.9	21.5	3.82	0.26	0.10	0.09	40	32	4	8	5	10	6	25.6	17.3	295	1535	1.67	1.20
Average	4.67	2.33	51.1	20.4	3.7	0.24	0.09	0.08	33	12	3	6	4	8	5	17.0	16.4	235	1498	1.32	0.68

TABLE 42: AVERAGED RATE OF CHANGE (PER TEN HOURS) DATA FOR TEST SERIES 2A, 2B, 2C, 3A, 3B, 3C, 3F.

OIL HOURS	TBN	TAN	VISC 20 C	VISC 40 C	VISC 100 C	CALCIUM	ZINC	PHOSPHORUS	IRON	COPPER	CHROMIUM	ALUMINIUM	LEAD	SODIUM	SILICON	BLACKNESS	% OIL CONS	OIL MAKE-UP	SUMP MASS	TOTAL I.M.	OXIDATION
	mg/g	mg/g	cSt	cSt	cSt	g/g	g/g	g/g	ppm	ppm	ppm	ppm	ppm	ppm	ppm	Absb		g	g	%	Integral
0	0.67	0.10	4.8	1.9	0.42	0.0210	0.0081	0.0076	1.98	0.20	0.10	0.30	0.20	0.50	0.40	0.00	0.00	0	150.0	0.00	0.000
10	-0.15	0.10	-0.4	-0.1	-0.07	-0.0005	0.0002	0.0003	0.20	0.28	0.03	0.13	0.35	0.17	0.25	0.70	1.99	0	-0.2	0.00	0.005
20	-0.05	-0.01	0.3	0.2	0.01	0.0007	0.0005	0.0002	0.20	0.10	0.02	0.03	-0.22	0.10	-0.18	0.31	-0.53	31	0.6	0.17	0.016
30	0.00	0.02	0.1	0.0	0.01	0.0010	0.0002	0.0000	0.42	0.08	0.03	0.02	-0.03	0.02	-0.05	0.29	0.21	-11	-3.0	-0.06	0.022
40	-0.02	0.03	0.2	-0.1	-0.01	0.0003	0.0002	0.0002	0.17	0.08	0.02	0.00	0.03	0.07	0.00	0.14	-0.15	6	1.2	0.03	-0.026
50	0.02	-0.01	0.3	0.1	0.00	0.0012	0.0003	0.0002	0.55	0.23	0.10	0.12	0.07	-0.05	0.03	0.21	0.04	-2	-0.4	-0.01	0.029
60	0.01	0.01	0.0	0.1	0.04	0.0005	-0.0002	0.0000	0.00	-0.02	-0.02	0.02	-0.07	0.08	-0.02	0.02	0.02	1	2.0	0.00	0.018
70	-0.04	0.00	0.0	0.0	-0.06	0.0008	0.0003	0.0002	0.38	0.13	0.05	0.08	0.03	0.03	0.02	0.27	-0.05	2	1.2	0.01	0.008
80	0.00	-0.02	-0.1	0.0	0.07	0.0008	0.0002	0.0002	0.17	0.15	0.00	0.03	-0.03	0.00	0.05	0.20	0.18	-5	-2.4	-0.03	0.023
90	0.02	0.03	0.2	0.1	-0.03	0.0005	0.0003	0.0003	-0.10	1.20	0.02	0.00	0.30	0.00	0.18	0.41	-0.12	6	0.7	0.03	0.105
100	0.01	0.00	0.0	0.0	0.00	-0.0002	-0.0002	-0.0002	0.00	0.72	0.02	0.02	-0.10	0.05	-0.05	0.00	0.12	1	3.9	0.01	-0.079
Average	-0.02	0.02	0.07	0.02	0.00	0.0005	0.0002	0.0001	0.20	0.30	0.03	0.05	0.03	0.05	0.02	0.26	0.17	2.95	0.4	0.02	0.012



TABLE 43: AVERAGED RATE OF CHANGE (PER HOUR) DATA FOR TEST SERIES 2A, 2B, 2C, 3A, 3B, 3C AND 3F.

OIL SERIES	TBN mg/g	TAN mg/g	VISC 20 C cSt	VISC 40 C cSt	VISC 100 C cSt	CALCIUM g/g	ZINC g/g	PHOSPHORUS g/g	IRON ppm	COPPER ppm	CHROMIUM ppm	ALUMINIUM ppm	LEAD ppm	SODIUM ppm	SILICON ppm	BLACKNESS Absb	% OIL CONS	OIL MAKE-UP g	SUMP MASS g	TOTAL I.M. %	OXIDATION
	(-)				(-)																Integral
2A	0.021	0.046	0.050	0.032	0.003	0.0005	0.0001	0.0001	0.310	0.040	0.020	0.030	0.020	0.070	0.010	0.283	0.187	2.910	1.010	0.018	0.006
2B	0.018	0.011	0.026	0.016	0.002	0.0004	0.0001	0.0001	0.070	0.020	0.010	0.020	0.010	0.040	0.000	0.163	0.199	4.160	0.020	0.023	0.018
2C	0.016	0.011	0.104	0.015	0.012	0.0007	0.0002	0.0002	0.060	0.010	0.020	0.040	0.040	0.020	0.010	0.293	0.240	2.450	0.020	0.014	0.013
3A	0.024	0.009	0.133	0.032	0.005	0.0006	0.0003	0.0002	0.430	1.410	0.050	0.090	0.110	0.100	0.100	0.417	0.226	4.590	0.870	0.026	0.015
3B	0.024	0.014	0.030	0.000	0.006	0.0004	0.0002	0.0002	0.110	0.150	0.020	0.030	0.020	0.020	0.010	0.158	0.131	2.520	0.900	0.014	0.009
3C	0.017	0.004	0.064	0.040	0.005	0.0005	0.0002	0.0002	0.000	0.210	0.150	0.060	0.000	0.030	0.010	0.221	0.059	1.060	1.030	0.006	0.011
3F	0.000	0.002	0.036	0.014	0.007	0.0004	0.0001	0.0001	0.007	0.005	0.003	0.004	0.015	0.005	0.007	0.027	0.192	1.056	3.207	0.012	0.007
AVERAGE	0.017	0.014	0.063	0.021	0.006	0.0005	0.0002	0.0002	0.141	0.264	0.039	0.039	0.031	0.041	0.021	0.223	0.176	2.678	1.008	0.016	0.011

## CHAPTER 6.

### 6. CONCLUSIONS AND IMPLICATIONS FOR FURTHER WORK.

#### 6.1 NEW OIL ANALYTICAL TECHNIQUES.

##### 6.1.1 Conclusions.

This work has developed three new oil analytical methods, namely, Total Base Number (for both IP 177 and IP 276), Total Insoluble Matter and Water Content. These new techniques have been shown to be superior to the standard methods in current use, in that they work well not only for new formulated oils, but also work equally well for used or severely abused oils, which is not the case for the standard oil analysis methods. The new basic techniques have been proven and shown to give excellent repeatability and reproducibility.

##### 6.1.2 Further Work.

The automated oil analyses for Total Base Number, Water Content and Total Insoluble Matter require further development of the systems and to tidy up the various processes of the system. This further development should also encompass a safety review and undertake robust system usage before the complete integrated instrument system can be considered for commercial production. Procedures for carrying out sample and solvent preparation along with glassware and instrument maintenance require review and documentation before the automated instrument can be further developed for marketing.

#### 6.2 USED OIL ANALYSIS FROM OPERATING DIESEL ENGINES.

##### 6.2.1 Conclusions of Oil Degradation.

The analysis of used oils from diesel engines revealed that the TBN and 100 °C oil viscosity decrease with the ageing of the oil. The TBN value of the new oil initially decreases rapidly followed by a less rapid change, suggesting that TBN is constituted from both fast and slow reacting additive. The oil viscosity at 20 °C and 40 °C increase with the ageing of the oil, together with calcium, oxidation level, wear metals and oil blackness. The trends of the oil analyses indicate that these parameters are being accumulated due to the selective removal of the light fractions of the base oil. The zinc and phosphorus levels have been found to accumulate at a lower rate than the

other elements, indicating that they are subject to an additional removal mechanism other than just the total loss method. The linear relationship between the Total Insoluble Matter (TIM) level and the Oil Make-up Mass level indicates the effect of oil dilution on TIM and the non-selective loss of TIM from the oil.

#### 6.2.2 Conclusions on Oil Degradation Model.

The oil degradation model previously proposed by Dyson [33] for the depletion of TBN has been verified. The Quasi-Continuous Stirred Tank Reactor Model has been shown to be a better model than the previously proposed Dyson model for modelling the degradation of lubricating oil. The QCSTR model allows the modelling of the lubricating oil degradation over the entire life of an engine as it considers both oil consumption and oil make-up in its treatment.

#### 6.2.3 Further Work.

The modelling of the lubricating oil degradation by the QCSTR model can be further enhanced by obtaining continuous on-line oil analyses and also without dismantling the engine at frequent intervals, which causes temporary disruption of the engines' system integrity.

#### 6.2.4 Other Further Work.

The area of great interest for future study is the need for a greater understanding and insight into top-ring zone chemistry and oil flow rates. This can be achieved by non-intrusive oil sampling from the top-ring zone. The current work has been limited by not having undertaken top-ring zone sampling in relation with the tests carried out. The current work does not consider the oil transfer (Maeda, Maeda and Yusotomi, [17] and degradation rates of the top-ring zone oil. The oil is understood to undergo severe degradation within the top-ring zone and such a study could also enable oil consumption mechanisms to be studied. This could possibly provide a complete understanding of oil degradation.

### 6.3 OTHER WORK.

If the characteristics in the top-ring zone could be understood, the task of linking lubricating oil degradation with engine wear would be more meaningful and a more accurate model would then be possible.

APPENDIX A

LEICESTER POLYTECHNIC,  
Conductimetric Determination of  
Total Base Number Using  
IP 177 or IP 276 Titrants.

Summary of Method.

The oil sample (0.5 g - 1.0 g) is dissolved in 40 cm<sup>3</sup> of the appropriate IP solvent mixture and is titrated conductimetrically with the respective IP acid (0.10 mol dm<sup>-3</sup>) using a standard conductivity cell. Conductance readings in the range 0 to 200 μS and 0 to 20 μS are noted depending on the respective IP method used. The end-point is determined from a plot of conductance readings against volume of titrant added.

Apparatus.

Conductance bridge (resolution 0.001 μS), glass conductivity cell, IP 276 type borosilicate glass beaker, burette (10 cm<sup>3</sup>, 0.02 cm<sup>3</sup> graduations), magnetic stirrer and magnetic follower.

Reagents.

Analar perchloric acid was used; all other IP reagents and solvents were of reagent grade. All solutions were prepared and standardised as stated in the respective IP methods.

Procedure.

The sample is stirred using a rotary-vibrator mixer for 30 seconds. A mass of oil is measured accurately to the nearest 0.1 mg and 40 cm<sup>3</sup> of solvent mixture added. The burette tip is immersed to just below the surface of the mixture and the conductivity cell placed such that no air bubbles are trapped inside the cell. Aliquots of 0.10 cm<sup>3</sup> are added at 30 second intervals, the conductance being recorded before the next aliquot is added. Titrant is added until a rapid and regular rise in conductance is observed. The end-point of the titration, V, for the IP 177 system corresponds to a discontinuity in gradient on a plot of conductance against volume of titrant added. The end-point for the IP 276 system corresponds to the second rapid change in the gradient of the curve. Typical curves obtained for both systems are shown in the graphs below.

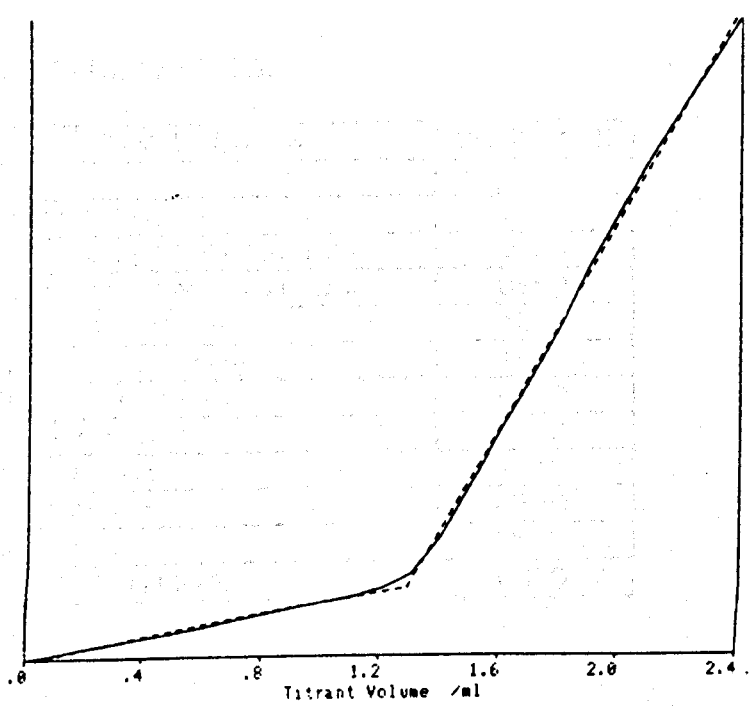
Calculation.

The Total Base Number (TBN), mg KOH g<sup>-1</sup> is calculated using the formula:

$$\text{TBN} = \frac{N \times V \times 56.11}{S}$$

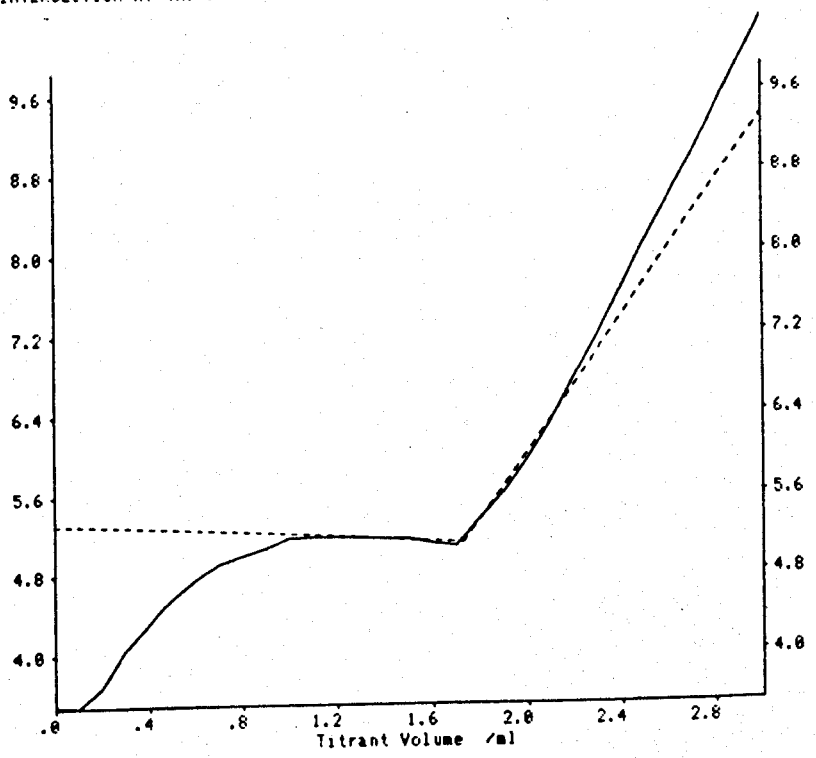
Where;  $N$  = Acid titrant concentration, mol  $\text{dm}^{-3}$   
 $V$  = Volume at end-point,  $\text{cm}^3$   
 $S$  = Mass of oil sample, g.

(a) IP 177 curve.



TBN = 9.4  
 INTERSECTION AT (X,Y) = ( 1.284, .172)

(b) IP 276 curve.



TBN = 9.3  
 INTERSECTION AT (X,Y) = ( 1.727, .510)



**ROUND ROBIN TEST OIL SAMPLES.**

<b>SAMPLE</b>	<b>SAMPLE ORIGIN</b>	<b>COMMENTS</b>
1	MOD ER5D (10W30)	NEW
2	MOD ER5D (10W30), 100 HOUR	USED
3	MOD ER5D (10W30), 250 HOUR	USED
4	BR 27/20264 (15W40)	NEW
5	BR 27/20450 (SAE40)	NEW
6	BR HST (SAE40)	USED
7	BR TBN (8 - 10)	USED
8	BR St. Anselm	NEW
9	BR St. Anselm	USED
10	BR Hengist	USED
11	BR HST Don (15W40)	USED

APPENDIX B: AUTOMATED TBN PROGRAMME.

```

1 TEXT:LET N$=STR$(+123):POKE 53272,PEEK(53272)OR2
2 DATA169,0,141,3,221,162,3,169,16,141,253,2,173,1,221,44,253,2,240,248,41,15
3 DATA9,48,157,252,127,202,14,253,2,16,235,96,8,72,173,0,221,77,252,2,141,0,221
4 DATA234,234,234,234,234,234,234,234,77,252,2,141,0,221,104,40,76,49,234,120,169,34
5 DATA141,20,3,169,204,141,21,3,88,96
6 FOR X=52224 TO 52299:READ Z:POKE X,Z:NEXT X
7 POKE$02FC,0:POKE$7FFC,$2B:DDR=56578:ADR=56576
8 POKE DDR,PEEK(DDR)OR12
9 POKE ADR,PEEK(ADR)AND2510R8
10 BLUE BORDER:L.GREY INK:SYS($CC3F)
20 DATA"  "
21 DATA"  "
22 DATA"  "
23 DATA"  "
24 DATA"  "
25 DATA"  "
26 DATA"  "
27 DATA"  "
28 DATA"  "
29 DATA"  "
30 DATA"  "
31 DATA"  "
32 DATA"  "
33 DATA"  "
34 DATA"  "
35 DATA"  "
40 DIM A$(15):FOR I=0 TO 15:READ A$(I):NEXT I
50 POKE $DD04,10:POKE $DD05,0:POKE $DD0E,149:POKE $DD0F,68
100 PRINT"OPTIONS AVAILABLE ARE :-"
110 PRINT"  1. -ILL SOLVENT BURETTE"
120 PRINT"  2. -ILL TITRANT BURETTE"
130 PRINT"  3. -ISPLAY CONDUCTANCE -.X.\."
140 PRINT"  4. -ERFORM FLOW TITRATION"
150 PRINT"  5. -LOT TITRATION CURVE"
160 PRINT"  6. -RINT RESULTS TABLE"
170 PRINT"  7. -XIT FROM PROGRAM"
180 PRINT"SELECT OPTION 1-2-3-4-5-6-7"
190 GET A$:IF A$="" THEN 190 ELSE Q=VAL(A$)
200 IF Q<1 OR Q>7 THEN 190 ELSE IF Q=7 THEN TEXT CLR:END
210 ON Q GOSUB 300,400,500,600,700,800:GOTO 100
300 INPUT"VOLUME REQUIRED/CM3":V:V=1000*V
310 D=4:IF V<0 THEN D=0
320 POKE ADR,PEEK(ADR)AND 251 OR D
330 V=ABS(V):POKE $02FC,8:T=TI
340 CALL DELAY(V):POKE $02FC,0
350 RETURN
400 INPUT"VOLUME REQUIRED/CM3":V:V=4608*V
410 D=4:IF V<0 THEN D=0
420 POKE ADR,PEEK(ADR)AND 251 OR D
430 V=ABS(V):POKE $DD06,250:POKE $DD07,0:POKE $DD0F,PEEK($DD0F)OR19:T=TI
440 CALL DELAY(V):POKE $DD0F,PEEK($DD0F)AND252
450 RETURN

```

```

500 PRINT "J":PRINT AT (24,1);"PRESS *↑* TO RETURN TO MENU";
510 REPEAT GOSUB 5000:GET A$:UNTIL A$=" "
520 RETURN
600 INPUT "SAMPLE NO. ";Q$
605 INPUT "TRANSPARENT MOLARITY (MOL/DM3)";M
610 INPUT "MASS OF OIL/100 CM3 SOLVENT";C
615 POKE ADR,PEEK(ADR)AND251:MAT R=ZER(40)
620 PRINT "PRESS *↑* TO START SOLVENT FLOW"
625 REPEAT GET A$:UNTIL A$=" "
630 POKE $02FC,8
635 CALL DELAY(600)
640 FOR I=4 TO 40:B=I/4
645 L=304362*M/C/B:H=INT(L/256):L=L-256*H
650 POKE $DD06,L:POKE $DD07,H:POKE $DD0F,PEEK($DD0F)OR19
655 T=TI:REPEAT SYS(52224)
660 PRINT AT (7,1);USING"-ONDUCTANCE READING = 'LLL,TBN =###.###",N$,B
665 UNTIL TI-T=600
670 R(I)=VAL(N$):NEXT I
675 POKE $DD0F,PEEK($DD0F)AND252
680 CALL DELAY(600)
685 POKE $02FC,0
690 RETURN
700 GRAPHICS CLR:L=R(1):S=L
710 FOR I=2 TO N:IF R(I)>L THEN L=R(I):ELSE IF R(I)<S THEN S=R(I)
720 NEXT I
730 PLOT(0,199*(R(1)-S)/(L-S))
740 FOR I=2 TO N:LINE TO ((I-1)*8,199*(R(I)-S)/(L-S)):NEXT I
750 REPEAT GET A$:UNTIL A$=" "
760 TEXT:RETURN
800 OPEN 1,4
810 PRINT#1," TBN      CONDUCTANCE"
820 IMAGE:###.###      ####
830 FOR I=4 TO 40
840 PRINT#1,USING 820,I/4,R(I)
850 NEXT I
860 CLOSE 1
870 RETURN
1000 DEF DELAY(J):T
1010 T=TI:REPEAT UNTIL TI-T=J
1020 RETURN
5000 SYS(52224)
5010 FOR J=1 TO 4:PRINT AT (10,8+4*J);A$(ASC(MID$(N$,J,1))AND15):NEXT J
5020 RETURN
6000 MAT D1=ZER(N-1):MAT D2=D1:FOR I=1 TO N-1:D1(I)=R(I+1)-R(I-1)
6010 D2(I)=R(I+1)-2*R(I)+R(I-1):NEXT I
6020 PRINT "J","R","D1","D2":PRINT 0,R(0)
6030 FOR I=1 TO N-1:PRINT I,R(I),D1(I),D2(I):NEXT I:PRINT N,R(N)
6040 GOTO 145

```

READY.

APPENDIX C: FULLY AUTOMATED TBN PROGRAMME.

\*\*\*\*\* TRIVECTOR BASIC Version 6.43 S \*\*\*\*\* 09:00:24 29/11/81  
( PR2/SYSMES : DLI / DLO : NDRAW : GRAPHICS : OSPC : TRANS )

```
1 C#=CHR$(21)&CHR$(31)
2 ?C#:"***** PLACE DATA DISK IN DRIVE 1 *****"
5 DIM Y(1000),H(21),C(4)
10 CALL SADLO,12
20 N#=""
30 FOR I=1 TO 23
40 N#=N#&CHR$(10)
50 NEXT I
60 FOR I=1 TO 79
70 N#=N#&CHR$(6)
80 NEXT I
95 V#=CHR$(10)&CHR$(8)&CHR$(8)&CHR$(8)&CHR$(8)&CHR$(8)
100 PRINT C#;
110 INPUT("TITRANT CONC. ")T0
114 PRINT
115 INPUT("OIL SAMPLE NAME ")U#
116 PRINT
117 INPUT ("VOLUME INCREMENT IN MICROLITRES ")P
118 PRINT
119 INPUT ("NUMBER OF STEPS REQUIRED ")N
120 PRINT C#;
130 R=1
140 C=10
150 GOSUB 10000
160 PRINT "OPTIONS ARE :- "
170 RESTORE 400
180 C=20
190 FOR R=4 TO 18 STEP 2
200 READ D#
210 GOSUB 10000
220 PRINT D#
230 NEXT R
240 R=22
250 C=10
260 GOSUB 10000
270 PRINT "SELECT 1 - 8"
280 INPUT CHARACTER O#
290 IF O#>"0" THEN IF O#<"9" THEN 310
300 GOTO 280
310 I=VAL(O#)
312 IF I>8 THEN 320
314 PRINT C#;
316 END
320 GOSUB 10000
330 PRINT"O.K. OPTION ";O#;" SELECTED"
340 ON I GOSUB 1000,2000,3000,4000,5000,6000,7000
350 GOTO 120
400 DATA "1. FILL BURETTE"
410 DATA "2. TITRATE"
420 DATA "3. PLOT TITRATION CURVE"
430 DATA "4. DISPLAY CONDUCTANCE"
440 DATA "5. PRINT RESULTS"
450 DATA "6. SAVE ON DISK"
460 DATA "7. LOAD FROM DISK"
470 DATA "8. END PROGRAM"
```

```

1000 PRINT C#:
1005 ?"***** BURETTE FILLING OPTION *****"
1006 PRINT
1010 INPUT (" HOW MANY MICROLITRES REQUIRED? ")N
1030 CALL SADLO,4
1060 FOR I=1 TO N
1070 CALL SADLO,0
1090 FOR J=1 TO 1
1090 NEXT J
1100 CALL SADLO,4
1110 FOR J=1 TO 1
1120 NEXT J
1130 NEXT I
1135 CALL SADLO,12
1140 RETURN
2000 PRINT C#
2009 PRINT "***** TITRATION OPTION *****"
2010 PRINT
2025 PRINT
2030 INPUT (" MASS OF OIL ")W
2040 CALL SADLO,13
2045 PRINT C#
2050 FOR Q=0 TO N-1
2070 GOSUB 13000
2080 FOR I=1 TO P
2090 GOSUB 8000
2100 NEXT I
2120 Y(Q)=Y
2122 LET R=2,C=72,F=6
2124 X#=" "&STR$(INT(Y*10^F))
2126 GOSUB 14140
2130 LET R=12,C=52,F=2
2140 X#=" "&STR$(Q)
2150 GOSUB 14140
2340 NEXT Q
2350 GOSUB 13000
2355 Y(N)=Y
2356 FOR J = 1 TO 2500
2358 NEXT J
2360 LET R=2,C=72,F=6
2370 X#=" "&STR$(INT(Y*10^F))
2380 GOSUB 14140
2390 LET R=12,C=52,F=2
2400 X#=" "&STR$(N)
2410 GOSUB 14140
2420 FOR I=1 TO 500
2430 NEXT I
2440 CALL SADLO,12
2450 GOSUB 12000
2500 FOR I= 0 TO N
2510 PRINTI*P/1000A2.30,Y(I)*1000A2.30
2520 NEXT I
2523 PRINT
2525 PRINT"PRESS ANY KEY TO RETURN TO OPTION PAGE"
2530 INPUT CHARACTER O#
2535 GOSUB 6000
2540 GOSUB 11000
2550 RETURN

```

```

3000 PRINT C$
3010 OPTION WIDTH 0
3020 X3=0*P/1000,X4=N*P/1000
3030 ?CHR$(29);CHR$(25);
3040 L=820,0=100,01=100,03=5,04=100
3050 GOSUB 45000 :REM Xaxis
3060 L=650,X3=Y0*1000,X4=Y9*1000
3070 GOSUB 45100 :REM LH Yaxis
3080 0=920,03=-5,04=-6,L=650
3090 GOSUB 45100 :REM RH Yaxis
3100 ?CHR$(29);
3110 X=01,Y=(Y(0)-Y0)/Y5*650+01
3120 CALL NDRAW,X,Y
3130 FOR I=1 TO N
3140 X=(I-X0)/N*820+01,Y=(Y(I)-Y0)/Y5*650+01
3150 CALL NDRAW,X,Y
3160 NEXT I
3161 ?CHR$(29);
3162 X=(M0-X0)/N*820+01,Y=(W0-Y0)/Y5*650+01
3163 CALL NDRAW,X,Y
3164 X=(M5-X0)/N*820+01,Y=(W5-Y0)/Y5*650+01
3165 CALL NDRAW,X,Y
3166 X=(M9-X0)/N*820+01,Y=(W9-Y0)/Y5*650+01
3167 CALL NDRAW,X,Y
3169 ?CHR$(29);
3170 INPUT CHARACTER 0$
3180 ?CHR$(24);
3200 RETURN
4000 CALL SPDL0,13
4003 PRINT C$
4005 ?"*****"***** DISPLAY OPTION SELECTED *****"
4010 R=8,C=72,F=6
4080 GOSUB 13000
4100 X$=" "&STR$(INT(1000000*Y))
4120 GOSUB 14140
4260 FOR Z=1 TO 500
4270 NEXT Z
4272 IF INPUT THEN 4290
4280 GOTO 4010
4290 CALL SPDL0,12
4300 GOSUB 11000
4310 RETURN
5000 PRINT C$
5010 OPTION WIDTH 0
5020 X3=0*P/1000,X4=N*P/1000
5030 ?CHR$(29);CHR$(25);
5040 L=950,0=70,01=-950,03=-5,04=70,A(3)=1
5045 ?!A(3),"SAMPLE NUMBER:- ";U$&A$
5046 ?!A(3)
5050 GOSUB 46000
5060 L=850,X3=Y0*1000,X4=Y9*1000
5070 GOSUB 46100
5080 0=1020,03=5,04=-5,L=850
5090 GOSUB 46100
5100 J=70,K=(Y(0)-Y0)/Y5*850+01
5110 ?!A(3),CHR$(2);"MX";JA4.00;"Y";KA4.00
5120 FOR I= 1 TO N
5130 J=I/N*950+70,K=(Y(I)-Y0)/Y5*850+01
5140 ?!A(3),"LX";JA4.00;"Y";KA4.00
5150 NEXT I

```

```

5151 J=M0/N*950+70,K=(W0-Y0)/Y5*850+01
5152 ?!A(3),CHR$(2);"MX";JA4.00;"Y";KA4.00
5153 J=M5/N*950+70,K=(W5-Y0)/Y5*850+01
5154 ?!A(3),"KX";JA4.00;"Y";KA4.00
5155 J=M9/N*950+70,K=(W9-Y0)/Y5*850+01
5156 ?!A(3),"KX";JA4.00;"Y";KA4.00
5157 J=70,K=01
5158 ?!A(3),CHR$(2);"MX";JA4.00;"Y";KA4.00
5160 ?!A(3),CHR$(13);CHR$(1)
5162 ?!A(3)
5163 ?!A(3),CHR$(27)&"4";"Titrant Volume /ml"
5164 ?!A(3)
5165 ?!A(3)
5166 ?!A(3),"TBN = ";56.11*M5*P*T0/1000/WA4.10
5167 ?!A(3)
5168 ?!A(3),"INTERSECTION AT (X,Y) = (";M5*P/1000A2.30;" ";"W5*1000A2.30;")"
5169 ?!A(3)
5170 FOR I= 0 TO N
5180 PRINT!A(3),I*P/1000,Y(I)*1000A2.30
5190 NEXT I
5200 INPUT CHARACTER 0#
5210 ?CHR$(24);
5220 RETURN
6000 PRINT C#
6005 A#=SUBSTR$(A#,2,5)
6007 F#=U$&A#
6010 ?"***** SAVING FILES ON DISK *****"
6020 S=1
6025 PRINT
6030 GOSUB 9000
6035 PRINT
6038 PRINTF#
6040 OPEN OUT#,TBN,DISC,RAN,F#
6050 FOR I=1 TO 21
6060 PRINT#TBN,H(I)
6070 NEXTI
6080 PRINT#TBN,T0,P,N,W
6090 FOR I=0 TO N
6100 PRINT#TBN,Y(I)
6110 NEXTI
6120 CLOSE #TBN
6130 RETURN
7000 REM
7005 PRINT C#
7010 PRINT "***** LOADING FILES FROM DISK *****"
7020 DIM H(21),Y(1000)
7030 S=0
7040 GOSUB 9000
7050 OPEN IN#TBN,DISC,RAN,F#
7060 FOR I=1 TO 21
7070 INPUT#TBN,H(I)
7080 NEXTI
7090 INPUT#TBN,T0,P,N,W
7100 DIM Y(1000)
7110 FOR I=0 TO N
7120 INPUT#TBN,Y(I)
7130 NEXTI
7133 CLOSE #TBN
7134 PRINT C#
7140 GOSUB 12000
7145 GOSUB 11000
7150 RETURN

```

```

8000 CALL SADLO,9
8010 FOR J=1 TO 1
8020 NEXT J
8030 CALL SADLO,13
8040 FOR J=1 TO 1
8050 NEXT J
8060 RETURN
9000 F1$="L"
9005 PRINT
9010 F=1
9040 F2$=SUBSTR$(F$,1,15)
9050 IF S=1 THEN 9080
9060 INPUT ("FILENAME ")F2$
9080 F$="&"&F2$
9090 RETURN
10000 REM POSITION CURSOR AT R,C
10010 PRINT CHR$(21);SUBSTR$(N$,25-R,R+C-2);
10020 RETURN
11000 OPTION WAIT ON,0
11001 PRINT C$
11004 ON ERROR GOTO 11015
11007 OPEN IN#TEN,STORE,RAN,"A"
11008 ON ERROR GOTO 11020
11010 SCRATCH#TBN
11014 GOTO 11020
11015 PRINT "UNABLE TO OPEN FILE"
11016 INPUT CHARACTER O$
11020 RETURN
11999 REM MAX-MIN IN Y
12000 PRINT C$
12005 ?"*****"***** CALCULATING T.B.N. *****
12008 Y0=Y(N),Y9=Y(N),Q=5,D=0
12010 FOR I=N-1 TO 0 STEP -1
12020 IF Y(I)<Y0 THEN Y0=Y(I)
12030 IF Y(I)>Y9 THEN Y9=Y(I)
12040 IF D<>0 THEN 12070
12050 IF Y(I+1)-Y(I)>=0 THEN 12070
12060 LET D=I
12070 NEXT I
12075 Y5=Y9-Y0
12080 IF D>=Q THEN 12110
12090 Q=Q-1
12100 GOTO 12080
12110 IF D<N-Q THEN 12140
12120 J=Q-1
12130 GOTO 12110
12140 FOR K=-1 TO 1 STEP 2
12150 LET S1=0,S2=0,S3=0,S4=0
12160 FOR I=0 TO Q
12170 J=D+K*I
12180 S1=S1+J
12185 S2=S2+J*J
12190 S3=S3+Y(J)
12200 S4=S4+J*Y(J)
12210 NEXT I
12220 C(3+K)=((Q+1)*S4-S1*S3)/((Q+1)*S2-S1*S1)
12230 C(2+K)=(S3-C(3+K)*S1)/(Q+1)
12240 LET D=D+1
12250 NEXT K
12260 LET M5=(C(1)-C(3))/(C(4)-C(2))
12270 LET W5=C(1)+C(2)*M5
12280 IF M5<0 THEN 12290
12281 IF M5>N THEN 12290
12282 IF W5>Y9 THEN 12290
12283 IF W5<Y0 THEN 12290
12285 K=1
12286 GOTO 12300
12290 K=0
12292 PRINT C$
12294 PRINT " INTERSECTION OUT OF RANGE ON PLOTTING"
12295 PRINT
12296 PRINT" PRESS SPACE BAR TO RETURN TO MAIN MENU"
12297 INPUT CHARACTER O$
12298 IF O$<>" " THEN 12297
12299 RETURN

```



```

12300 M0=0, W0=C(1), M9=N, W9=C(3)+M9*C(4)
12305 IF W0<Y0 THEN 12307
12306 GOTO 12310
12307 W0=Y0, M0=(Y0-C(1))/C(2)
12310 IF W9>Y9 THEN 12315
12311 GOTO 12330
12315 W9=Y9, M9=(Y9-C(3))/C(4)
12330 PRINT C#
12340 PRINT"INTERSECTION AT (":M5*P/1000#2.3U":",":W5*1000#2.3U":")"
12344 PRINT
12345 PRINT "X0 = ":M0#2.0U,"Y0 = ":W0*1000#2.3U
12346 PRINT
12348 PRINT "XL = ":M9#2.0U,"YL = ":W9*1000#2.3U
12350 PRINT
12360 PRINT"T.B.N. = ":56.11*T0*P*M5/W/1000#2.1U
12365 PRINT
12370 PRINT "PRESS ANY KEY TO CONTINUE"
12380 INPUT CHARACTER O#
12390 RETURN
13000 OPTION WAIT ON,2
13010 OPEN IN#TBN,STORE,RAN,"A"
13020 SAMPLE1#TBN,H,A#
13030 RESTORE #TBN,H(9)
13040 INPUT#TBN,Y
13050 CLOSE#TBN
13060 RETURN
13984 DATA " ", " ", " ", " ", " ", " ", " ", " ", " ", " "
14000 DATA" 000 ", "0 0", "0 0", "0", "0 0", "0", "0 0", "0", "0 0", "0", "000 "
14001 DATA" 1 ", "1 1", "1", "1", "1", "1", "1", "1", "1", "11111"
14002 DATA" 222 ", "2 2", "2", "2", "2", "2", "2", "2", "2", "22222"
14003 DATA" 333 ", "3 3", "3", "3", "3", "333", "3", "3", "333 "
14004 DATA" 4", "44", "4 4", "4 4", "4 4", "44444", "4", "4"
14005 DATA"55555", "5", "5", "5555", "5", "5", "5", "555 "
14006 DATA" 6 ", "6", "6", "6666", "6", "6", "6", "666 "
14007 DATA"77777", "7", "7", "7", "7", "7", "7", "7"
14008 DATA" 888 ", "8 8", "8 8", "8", "888", "8 8", "8", "888 "
14009 DATA" 999 ", "9 9", "9 9", "9", "9999", "9", "9", "9 "
14140 FOR X=LEN(X#)-1 TO LEN(X#)-F STEP -1
14150 LET C=C-10
14160 GOSUB 10000
14170 L=13952+ASC(SUBSTR$(X#,X,1))
14180 RESTORE(L)
14190 FOR Z=1 TO 7
14200 READ Z#
14210 PRINT Z#:V#;
14220 NEXT Z
14230 NEXT X
14240 RETURN
40000 REM Plot axes. Set up L,0,01,03,04,X3=min,X4=max data value
40010 X7=X4-X3,D1=.01:REM X3=MIN,X4=MAX
40020 GOSUB 40000:REM Range >.1
40030 X5=D1/10,D2=X5*INT((X3/X5)+.999999999),D3=(L*X5)/X7,X#=STR$(X5)
40040 GOSUB 40130
40050 V=X(0)-I-1,X#=STR$(X4):REM V=number chars after decimal
40070 GOSUB 40130
40090 V=(I-2)*10+V
40100 IF X3=0 THEN IF V<10 THEN V=V+10
40105 RETURN
40130 CHANGE X# TO X
40140 IF X(0)>12 GOTO 40180
40150 FOR I=1 TO X(0)
40160 IF X(I)=46 THEN RETURN
40165 NEXT I
40170 X(0)=X(0)+1,I=I-1
40175 RETURN
40180 I=VAL(SEG$(X#,14,15)),X(0)=I*2+1
40185 RETURN

```

```

40200 REM Plot x axis
40205 D4=D3/X5*(D2-X3)+0,L=L+1
40210 ?CHR$(29);
40220 CALL NDRAW,0,01
40240 FOR I=D4 TO L STEP D3
40250 CALL NDRAW,I,01
40255 O1=O1-O3
40260 CALL NDRAW,I,01
40265 O1=O1+O3
40270 CALL NDRAW,I,01
40280 NEXT I
40290 CALL NDRAW,L,01
40295 RETURN
40400 REM Plot y axis
40405 D4=D3/X5*(D2-X3)+01,L=L+01
40410 ?CHR$(29);
40420 CALL NDRAW,0,01
40440 FOR I=D4 TO L STEP D3
40450 CALL NDRAW,0,I
40455 O=O-O3
40460 CALL NDRAW,0,I
40465 O=O+O3
40470 CALL NDRAW,0,I
40480 NEXT I
40490 CALL NDRAW,0,L
40495 RETURN
40800 O=O1
40810 IF X7<=0 THEN RETURN
40820 O1=O1+O,O=O*2
40830 FOR J=1 TO 4
40840 IF X7<=O1 THEN RETURN
40850 O1=O1+O
40860 NEXT J
40870 GOTO 40800
40899 REM Label x axis
40900 O2=O1-35,D=O2
40905 IF O2<0 THEN O2=0
40915 FOR I=D4-50 TO L-50 STEP D3
40920 ?CHR$(29);
40930 CALL NDRAW,I,02
40940 ?CHR$(31);DAVU;
40950 O=O+X5
40960 NEXT I
40970 RETURN
41000 REM Label y axis
41010 O2=O-04,D=O2
41020 IF O2<0 THEN O2=0
41025 IF O2>1000 THEN O2=1000
41040 FOR I=D4 TO L STEP D3
41050 ?CHR$(29);
41060 CALL NDRAW,02,I
41070 ?CHR$(31);DAVU;
41080 O=O+X5
41090 NEXT I
41100 RETURN

```

```

42999 REM Text to screen
45000 GOSUB 40000
45010 GOSUB 40200
45020 GOSUB 40900
45030 RETURN
45100 GOSUB 40000
45110 GOSUB 40400
45120 GOSUB 41000
45130 RETURN
46000 GOSUB 40000
46010 GOSUB 60200
46020 GOSUB 60900
46030 RETURN
46100 GOSUB 40000
46110 GOSUB 60400
46120 GOSUB 61000
46130 RETURN
60200 D4=D3/X5*(D2-X3)+0,L=L+0
60220 ?!A(3),CHR$(2);"SMX";0A3.00;"Y";01A4.00
60240 FOR I=D4 TO L STEP D3
60260 ?!A(3),"LX";IA4.00;"Y";01A4.00;"LU0V";03A2.00;"LU0V";-03A2.00
60270 NEXT I
60280 ?!A(3),"LX";LA4.00;"Y";01A4.00;CHR$(13);CHR$(1)
60290 RETURN
60399 REM Plot y axis
60400 D4=D3/X5*(D2-X3)+01,L=L+01
60420 ?!A(3),CHR$(2);"MX";0A4.00;"Y";01A4.00
60440 FOR I=D4 TO L STEP D3
60460 ?!A(3),"LX";0A4.00;"Y";IA4.00;"LU";03A2.00;"V0LU";-03A2.00;"V0"
60470 NEXT I
60480 ?!A(3),"LX";0A4.00;"Y";LA4.00
60485 ?!A(3),CHR$(1);
60490 RETURN
60900 O2=01-20,D=02
60920 FOR I=D4-50 TO L-50 STEP D3
60930 ?!A(3),CHR$(2);"MX";IA4.00;"Y";02A4.00
60940 ?!A(3),CHR$(1);DAVU
60950 D=D+X5
60960 NEXT I
60970 RETURN
61000 REM Label y axis
61010 O2=0-04,D=02
61020 IF O2<0 THEN O2=0
61030 IF O2>1020 THEN O2=1020
61040 FOR I=D4 TO L STEP D3
61050 ?!A(3),CHR$(2);"MX";02A4.00;"Y";IA4.00
61060 ?!A(3),CHR$(1);DAVU
61070 D=D+X5
61080 NEXT I
61090 ?!A(3),CHR$(2);"MX";02A4.00;"Y";01A4.00
61100 ?!A(3),CHR$(1);
61110 RETURN

```

APPENDIX D: UNATTENDED ENGINE MONITORING AND CONTROL

PROGRAMME.

```

10 LET F$="XXXXXXXXXXXXXXXXXXXXXXXXXXXX"
20 FOR COL=1 TO 40:F$=F$+" ":NEXT COL
30 DIM L(9),D0(9),D1(9),A$(9),V(1,5,9)
40 FOR I=1 TO 9
50 READ A$(I),L(I),D0(I),D1(I)
60 NEXT I
70 REM CLEAR BACKUP MEMORY
80 W=0:M=40984
90 FOR I=M TO 42887:POKE I,0:NEXT I
100 POKE 59459,0:POKE 59458,PEEK(59458)OR24:POKE 59468,236:SYS(58638)
110 POKE 59456,PEEK(59456)AND231
190 INPUT"TIME IN HOURS:MINUTES :-";B$
200 INPUT"REF. TEMP :-";Z
210 INPUT"DATAFILE NAME :-";F$
220 INPUT"ENGINE 0 DURATION(HRS):-";D(0):D(0)=216000*D(0)
230 INPUT"ENGINE 1 DURATION(HRS):-";D(1):D(1)=216000*D(1)
240 POKE 59456,PEEK(59456)OR8*(SGN(D(0))+2*SGN(D(1)))
250 PRINT"NOW START THE ENGINE(S)"
260 PRINT"WHEN READY PRESS SPACE BAR"
270 GET A$:IF A$(">") THEN 270
280 FR=0:SS=0:TI$="000000":PRINT" ";TAB(19);"ENGINE 0 ENGINE 1"
290 FOR I=1 TO 9:ROW=2*(I+1):COL=1:GOSUB6000:PRINT A$(I):NEXT I
300 IF D(0)=0 AND D(1)=0 THEN SS=1
305 PR$=MID$(TI$,3,1):IF PR$="2" OR PR$="5" THEN PR=0
310 FOR E=0 TO 1:E$="ON"
320 IF D(E)=0 THEN E$="OFF"
330 ROW=3:COL=23+12*E:GOSUB 6000:PRINT E$:COL=21+12*E:GOSUB 5000
340 FOR Q=1 TO 8
350 IF E$="OFF" THEN Q=8:GOTO 450
360 ROW=2*(Q+1):GOSUB6000:PRINT" "
370 GOSUB 6000:POKE 59468,236:POKE59468,204:V(E,5,Q)=PEEK(59471)
375 ON Q GOTO 385,385,380,385
380 R(E,Q)=INT(V(E,5,Q)*L(Q))/10+Z:PRINTR(E,Q):GOTO390
385 R(E,Q)=INT(V(E,5,Q)*L(Q))/10:PRINTR(E,Q)
390 J=0
400 FOR K=1 TO 5
410 IF V(E,K,Q)<D0(Q)ORV(E,K,Q)>D1(Q) THEN J=J+1
420 LET V(E,K-1,Q)=V(E,K,Q)
430 NEXT K
440 IF J=5 THEN GOSUB 6000:PRINT" ";INT(V(E,5,Q)*L(Q))/10:D(E)=0:E$="OFF"
450 NEXT Q
460 IFE$="ON"THENROW=20:GOSUB6000:PRINT" ":GOSUB6000:PRINTINT(TI/216)/1000
470 IF TI>D(E) THEN D(E)=0
480 NEXT E
485 IF PR=0 AND (FR$="0" OR FR$="3") THEN GOSUB 7000:FR=1
490 IF SS=0 THEN 300
500 ROW=22:COL=1:GOSUB6000
550 GOSUB 7000
600 GOSUB 8000
999 END

```

```

3000 REM DATA
3010 DATA "SPEED(RPM)      ",157,0,256
3020 DATA "OIL PRESS(BAR)  ",0.255,-1,256
3030 DATA "OIL TEMP(C)    ",5.39,-1,256
3040 DATA "LOAD(KW)       ",0.1277,-1,256
3050 DATA "BREATHER TEMP(C)",5.53,-1,256
3060 DATA "EXHAUST TEMP(C)",18.7,-1,256
3070 DATA "CYL HEAD TEMP(C)",9,-1,256
3080 DATA "ROOM TEMP(C)   ",1.56,-1,256
3090 DATA "ELAPSED TIME(HR)",0,0,0
5000 REM ENGINE CONTROL
5010 FOKE 59408,PEEK(59408)AND(255+32*(E$="ON"))OR(-32*(E$="OFF"))
5020 FOKE 59456,PEEK(59456)AND(255+16*(E=1))OR(-16*(E=0))
5030 FOKE 59456,PEEK(59456)AND247
5040 FOKE 59456,PEEK(59456)OR8
5050 RETURN
6000 REM POSITION CURSOR AT ROW,COL
6010 PRINT" ";MID$(P$,26-ROW,ROW+COL-2);
6020 RETURN
7000 FOR E=0 TO 1
7010 FOR Q=1 TO 8
7020 FOKE(E*1024+M+Q+W),V(E,5,Q)
7030 NEXT Q:NEXT E
7040 W=W+8
7050 RETURN
8000 INFUT"ENGINE NUMBER FOR PRINTOUT ";P
8005 E=P-2;TS=BS;MM=(40984+E*1024)
8008 OPEN 4,4;CMD4
8010 PRINT,CHR$(14) "          RESULTS";CHR$(4);CHR$(10)
8020 PRINT
8030 PRINT"TEST NO. ";F$
8040 PRINT
8050 PRINT"ENGINE ";P
8060 PRINT"*****";
8070 PRINT"*****";
8080 PRINT" * SPEED * OIL * OIL * LOAD * BLOWBY * EXHAUST *";
8090 PRINT" * HEAD * ROOM * TIME *";
8100 PRINT" * R.P.M * PRESS * TEMP * KW * TEMP * TEMP *";
8110 PRINT" * TEMP * TEMP * HR:MIN *";
8120 PRINT"*****";
8130 PRINT"*****";
8140 PRINTCHR$(27);"D";CHR$(8);CHR$(16);CHR$(24);CHR$(32);CHR$(41);
8150 PRINTCHR$(51);CHR$(59);CHR$(67);CHR$(76);CHR$(8)
8160 H$=CHR$(9)
8180 PRINT"*";INT(PEEK(MM+1)*15.7+.5);
8190 PRINTH$;"*";(INT((PEEK(MM+2)/39.2)*100+.5))/100;
8200 PRINTH$;"*";((INT(PEEK(MM+3)/1.855+.5)*100)/100)+Z;
8210 PRINTH$;"*";(INT((PEEK(MM+4)*12.77/1000)*100+.5))/100;
8220 PRINTH$;"*";((INT(PEEK(MM+5)/1.81+.5)*100)/100)+Z;
8230 PRINTH$;"*";INT(PEEK(MM+6)*1.87+.5)+Z;
8240 PRINTH$;"*";INT(PEEK(MM+7)/1.111+.5)+Z;
8250 PRINTH$;"*";INT(PEEK(MM+8)/6.42+.5)+Z;
8260 PRINTH$"*";TS;
8270 PRINTH$"*";
8280 IFMM>(42008+E*1024)THEN 8380
8290 TS=TS+30;AS=INT((TS/100))*100
8300 FS=TS-AS
8310 IF FS>=60THENTS=AS+100+(FS-60)
8320 IFTS>=2400THENTS=TS-2400
8330 J=0;FOR I=1 TO 8:IF PEEK(MM+I)=0 THEN J=J+1:NEXTI
8340 IF J=8 THEN 8380
8350 MM=MM+8
8360 GOTO 8140
8370 PRINTCHR$(10);
8380 PRINT:PRINT"*****";
8390 PRINT"*****"
8400 PRINT:PRINT
8410 PRINT#4;CLOSE4
8420 GOTO 6000
8440 END

```



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DEDICATED TO AUTOMATION

# CM4000 Automated Oil Analyser



## Total Base Number

Hydrochloric or  
Perchloric Acid  
Conductimetric  
Titrations

## Total Insoluble Matter

Infra-Red  
Absorption  
Technique

## Water Content

Novel  
Vapour  
Pressure  
Method



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Laboratory  
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Systems



**T**hree important parameters in Oil Condition Monitoring automatically determined in one unit, with a through-put of up to 15 samples/hour unattended operation:

### Total Base Number (TBN)

This determination indicates the relative amount of active additive remaining in an engine oil to neutralise acidic by-products generated during combustion.

Determination is carried out by precision titration under software control. The titration itself is done using traditional neugents (according to IP177/ASTM D664 or IP276/ASTM D896), the titration

rate being programmable from 1-100  $\mu$ l/sec. Accurate sample volumes are achieved using loop-fill techniques. A conductimetric end-point determination is made giving outstanding precision over a wide range of new and used oils without the necessity for back-titration. Results, including the option to plot each individual titration curve, are clearly shown on the printer.

### Water Content

In this analysis a vapour pressure technique is used in parallel with the TBN determination. An accurately defined sample volume in a sealed PTFE tube is heated to a pre-selected temperature, approximately 150°C,

at a defined programmable rate. The pressure in the head-space is monitored and automatically compared to a standard calibration curve.

### Total Insoluble Matter

Following TBN analysis the sample may be transferred to a tube of approximately 0.5mm pathlength. A technique of infra-red absorption at a wavelength of 880nm is used for the actual determination. To compensate for optical and electronic drift, both blank and dark current corrections are carried out on each sample. Results are compared with pre-calibrated standards.

## Specification

### General

Basic unit comprising:

- 16 bit, 10MHz processor with real time clock
- High resolution conductivity circuit
- 0.5 Mbyte DRAM, 128K ROM
- Optical detectors with adjustable light sources and variable gain
- Unique multi-tasking and diagnostic software
- Temperature control and measurement

- Visual Display Unit
- High resolution pressure transducer
- 40 or 100 position autosampler

### Total Base Number

Range 1-60mg KOH/ml overall  
Resolution 0.1 mg KOH/ml  
Repeatability 1%

### Water Content

Range 0.1% - 2%

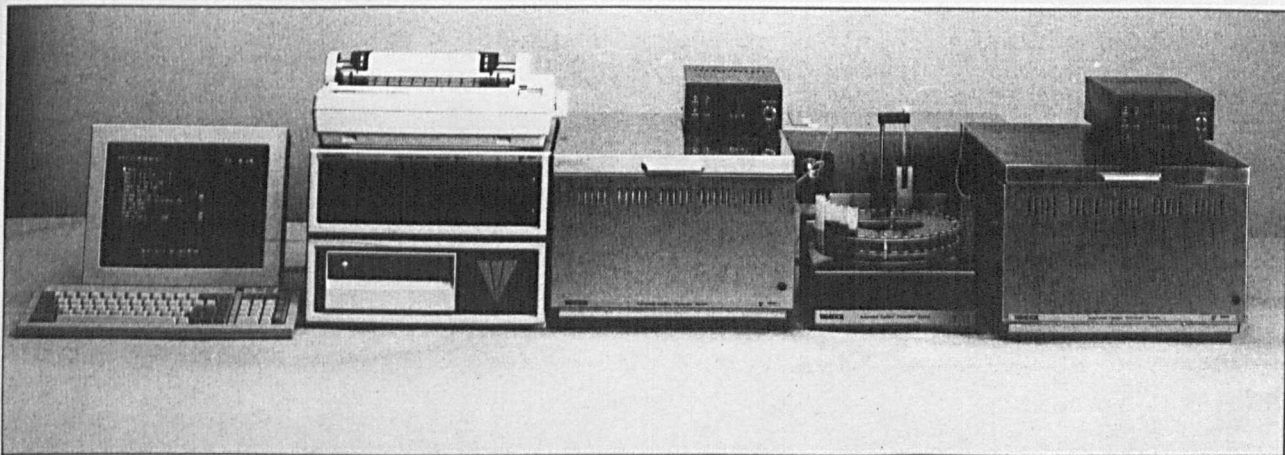
Resolution 0.1%  
Repeatability 5%

### Total Insoluble matter

Range 0.1% - 10% (variable)  
Resolution 0.1%  
Repeatability 5%

In addition to the CM4000 Automated Oil Analyser Trivector Systems International Limited also manufacture:

## The CM4500 Automated Capillary Viscometer



For the determination of viscosity in the range 5 to 500 cPs at 40°C or 1 to 50 cPs at 100°C with viscosity index if required.

In addition to these, Trivector market the ISL range of oil analysis equipment as follows:

- Cold Filter Plugging Point
- Automatic Pensky-Martens Apparatus
- Automatic Cleveland Apparatus
- Automatic Apparatus for Cloud Point and Pour Point Measurement
- Automatic Cleveland Apparatus with Sample Changer
- Automatic Softening Point Determination Ball and Ring Method
- Automatic Vacuum Distillation Apparatus
- Automatic Flash Point Measurement
- Automatic Distillation (D86)
- Semi-Automatic Reid Vapour Pressure Equipment

**TRIVECTOR**

DEDICATED TO AUTOMATION

Trivector Systems International Limited  
Sunderland Road, Sandy, Bedfordshire SG19 1RB England.  
Telephone: Sandy (0767) 82222 Telex: 825478 TRISYS G.

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**Computer  
Systems**

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