ADDITIVES FOR LUBRICANTS

BY

G. H. THORNLEY

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INTRODUCTION

BY

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The subject of additives in lubricating oils is one which can hardly have escaped the attention of engineering personnel at sea today in steam turbine and Diesel-driven ships and craft.

Accordingly, Mr. Thornley's article should be of widespread interest in giving a general picture of recent developments and a background against which to view the recent rather bewildering sequence of changes of lubricating oil specifications, especially for Diesel engines.

The warning must be given that developments since 1958, when this article was written, make it dangerous to assume that all the additive chemicals mentioned are still necessarily used today and it must, of course, also be realized that all the major lubricating oil companies are active in this field.

ADDITIVES FOR LUBRICANTS

In 1955 rather more than one and a quarter million tons of lubricating oil additives were manufactured, and presumably sold. In 1956, the total rose to 1,350,000 tons, and the estimate for 1960 is rather more than one and a half million tons. These quantities can be roughly estimated as to approximately 50 per cent detergents, 25 per cent viscosity index improvers, and 11 per cent anti-oxidants ; pour point depressants, extreme pressure lubricant additives, oiliness additives and the like, totalling together about 14 per cent.

Additives are put into lubricating oils for a great variety of purposes. The oil in the internal combustion engine has principally to do two things—to reduce friction, and to carry away heat. To do this it is churned through the oil pump, pushed through narrow passages under pressure, sprayed out of the ends of bearings in fine mist, and spread in thin films on hot metal. Heat and flame and oxidizing gases assail it ; it is contaminated with soot, aldehydes, gaseous and liquid acids, steam and liquid water, and from petrol engines using leaded fuel, chlorine, bromine, and lead compounds. It must present an incorruptible front to these assaults. Therefore its stability is very important, and additives do a great deal to improve the stability of the petroleum which nature and the refiner produce.

Anti-oxidants help to prevent chemical deterioration of the oil. Detergents combat the evil effect of solid decomposition products from fuel and lubricant. Viscosity index improvers alleviate the physical effect of temperature change on viscosity. Pour point depressants prevent solidification due to inter-locking of wax crystals when the oil is cooled.

TABLE I

CLR OIL TEST ENGINE

L-38 Procedure

Test duration, hours	40
Speed, revs/min	3,150 ± 25
Load, b.h.p.	5·0 approx.
Fuel	PE/IP L-4 Ref. gasoline
Fuel consumption, lb/hr	4·5–5·0
Air fuel ratio	14·0 ± 0·5/1
Intake air temp., degrees F.	80 min.
Jacket outlet temp., degrees F.	200 ± 2
Outlet temp. above inlet temp., degrees F.	10 ± 1
Oil gallery temp., degrees F.	280 ± 2(SAE 10–265 ± 2)
Spark advance degrees b.t.d.c.	35 ± 1
Oil pressure, lb/sq in.	40 ± 2
Crankcase vacuum, inches water	2 ± 0·5
Exhaust back pressure, inches mercury	0/1

Anti-Oxidants

Anti-oxidants are oil soluble organic compounds or metallo-organic compounds of four principal types. First, sulphur compounds : sulphurized esters, sulphurized terpenes and olefins, aryl and alkyl phenol sulphides, and metallo dithio-carbonates. Second, phosphorus compounds : alkyl or aryl phosphites, or the naturally occurring compound lecithin. Third, sulphur and phosphorus compounds : metal salts of dithio-phosphoric acids made by reacting alcohols with phosphorus pentasulphide, or reaction products of terpenes with phosphorus sesquisulphide. Fourth, amines and phenolic compounds—which are not very useful in internal combustion engine oils where high temperatures prevail, but are very good anti-oxidants for moderate temperature work.

The well known oiliness characteristics of castor oil are particularly useful for racing engines, and for lubrication of worm-gearing, and other highly-stressed machinery, but uninhibited castor oil is easily oxidized, and its oxidation products readily polymerize into undesirable gums and other solid products. A suitable combination of anti-oxidants can effect most spectacular improvement in resistance of castor oil to oxidation and gum formation.

A great variety of laboratory tests to evaluate these anti-oxidants have been devised over the last thirty or forty years, but they are not entirely adequate, and we are forced to more expensive engine tests, such as the L-4 Chevrolet test which was devised in the United States about 1940 and has held sway in official specifications ever since. It uses a 6-cylinder engine and is, therefore, relatively expensive to run, so endeavours are made to find a simpler engine which will operate at less cost. In the United States the Co-ordinating Research Council, Co-operative Lubricants Research Section, has, after a great deal of co-operative work between engine manufacturers and the petroleum industry, brought out the CLR (Co-operative Lubricants Research) engine, which is intended to replace the Chevrolet. This is a single-cylinder, robust engine, designed specifically for lubricants testing, for ease of assembly and disassembly, for flexibility, and for ability to hold constant operating conditions.

The proposed test procedure for the CLR engine is known as the L-38 procedure and is shown in TABLE I.

In the United States the CLR engine was devised purely as an oil test engine, whereas Britain, co-operatively, took an existing engine already in production and fairly cheap to buy, made certain modifications to it, and set up a procedure as shown in TABLE II. The Engine Testing of Lubricants Panel of the IP

TABLE II

PETTER W-1 OXIDATION TEST PROCEDURE

Operating time, hours	36
Speed, revs/min	1,500 ± 15
Load, b.h.p.	3·3 approx.
Oil pressure, lb/sq in.	8 ± 3
Oil temperature:	
SAE 20, 30, 40 and 50, degrees F.	280 ± 2
SAE 10, degrees F.	266 ± 2
Coolant temperature inlet, degrees F.	299 ± 4
Coolant temperature outlet, degrees F.	302 ± 2
Hot-spot heater plate temperature, degrees F.	392 ± 9
Spark advance, degrees b.t.d.c.	20 ± 1
Oil capacity, pints	2
Fuel	PE/IP L-4 Ref. gasoline
Fuel flow	45·2 sec for 20 ml ± 0·5 sec.

Standardization Committee carried out co-operative research with a view to finding a procedure with the Petter W-1 engine to replace the Chevrolet at much lower initial and test running costs.

In the 36-hour Chevrolet L–4 test with an oil sump temperature of 280 degrees F, most mineral oils will give lacquered pistons with stuck rings and connecting rod bearing weight losses of over 1,000 mg. Additive treated oils of DEF.2101 quality give clean pistons with free rings and bearing weight losses below 200 mg, and often well below 100 mg. The value of oxidation inhibitors in reducing bearing weight loss caused by oil oxidation products is shown by the fact that a bearing weight loss of the order of 2,000 mg can be reduced to less than 50 by the addition of little more than 0·5 per cent of a suitable anti-oxidant to the oil.

Very similar comparative results are obtained from the Petter W-1 test and correlation with the L–4 test may well be a possibility.

Detergents

Having dealt briefly with anti-oxidants, we come to detergents, or detergent-dispersant additives. These come in many varieties. Invariably there is a metal, calcium, barium, magnesium, aluminium, or tin with a coupling group, sulphonate, hydroxyl, carboxyl, or mercaptan between the metal and the organic component. There is generally in the structure a high molecular weight, straight or branched paraffin chain, or aromatic or naphthene rings to promote oil solubility. These detergent additives can be over-based, or made basic. This can be done by taking, for example, a barium petroleum sulphonate, incorporating more barium into the compound than the neutral barium petroleum sulphonate formula requires. This extra basicity is of value in combating the evil effects of sulphur acids from the combustion of high sulphur fuels in compression ignition engines. The detergent additives are quite often pro-oxidants in themselves, so that they are almost invariably used in conjunction with anti-oxidants.

For testing for detergency in the laboratory, tests can be conducted with suspensions of carbon black, examining the degree of dispersion with dispersant additives, but it is imperative to do engine tests, and the well-known Caterpillar L–1 test, which forms part of military and other specifications all over the world, is that most generally used. It is a 480-hr. test with an expensive engine. The Caterpillar L–1 test forms part of DEF-2101, the U.S. MIL-L-2104A, and other official specifications. Fuel of minimum sulphur content 0·35 per cent is used in this test. If the test is similarly carried out, but with fuel of 1 per cent sulphur

TABLE III

FL-2 PROCEDURE

Engine	Chevrolet
Operating time (total), hours	40
Speed, revs/min	2,500 ± 25
Load, b.h.p.	45 ± 1
Coolant outlet temperature, degrees F.	100 ± 5
Coolant inlet temperature, degrees F.	90 ± 2
Sump oil temperature, degrees F.	165 ± 5
Air-fuel ratio	14·5 ± 0·5/1
Initial oil fill, lb	7½
Oil make up	At 20 hours

content, we get what is known as the Supplement I test, and a distinctly superior degree of detergency is required to cope with the higher sulphur content of the fuel. For the Caterpillar Company's requirements, the Series 2 oil again uses the Caterpillar 480-hr test and a 1 per cent sulphur fuel, but with a supercharged engine, which makes conditions in the piston ring area much more arduous and requires a higher degree of detergency. The Caterpillar Company now specify a Series 3 oil, for which an even higher degree of supercharging makes conditions much worse, and again, more additive is required.

Naturally, therefore, people have looked for smaller engines with tests of shorter duration, to save cost. Examples are the Lauson engine, and the Petter AV–1. Lauson and Petter AV–1 engine test procedures have been devised which rate oils in somewhat similar order to the Caterpillar L–1 procedure, but the correlation is still far from complete.

The mechanism of detergency — keeping engines clean by suspending or peptizing sludge — is a mainly physical action, but there is probably a chemical effect also. The chemical action of over-based detergents in neutralizing sulphur acids from the combustion of high sulphur fuel has been mentioned, but in addition there is oxidation of hydrocarbons producing oxygenated acids from either the fuel or the lubricant. These acids have a limited solubility in mineral oils, and are liable to polymerize in the hotter parts of the engine to form lacquer and carbonaceous deposits.

The metallic salts used as detergent additives may be considered basic towards the oxygenated acids, so that a reaction occurs forming a complex oxy-acid, for example naphthenate or sulphonate salt, which is oil-soluble and does not readily polymerize. Many detergent additives increase the foaming tendency of oils, and it is fortunate that anti-foam additives are available which completely overcome this defect.

Additives for Low Temperature Conditions

So far consideration has been given to internal combustion engine oil additives for high-temperature operation, but for low-temperature conditions the problems are quite different. Dr. C. G. Williams was the first to propound, more than twenty years ago, the corrosive theory of cylinder wear, which is now universally accepted : that at any temperatures below about 55–60 degrees C in the combustion chamber there will be condensation of water of combustion. In addition to the fact that the combustion of a gallon of petrol produces rather more than a gallon of water, there are carbon, sulphur, and nitrogen oxides which, in the presence of water, form corrosive acids. Oils tend to be thick when they are cold, so in cold starting there is the lowest rate of oil circulation when it needs the quickest rate to cover the surfaces and protect them, either by neutralizing acids or by laying down protective films which will prevent

TABLE IV

THE EX-2 PROCEDURE

Engine .. .. Chevrolet (as for FL-2)
Modifications to standard engine:
1. Rocker cover vents welded shut
2. 4 vertical notches in top compression rings 0·125 in. wide × 0·009 in. deep
Narrow slot (1/32 in.) oil rings in pistons 1, 3 and 5
All lands chamfered
Operating time (total) .. .. 96 hours

Details of cycle	*Time, hours*	*Speed, revs/min*	*Load, b.h.p.*	*Coolant outlet temp., degrees F.*	*Oil temp., degrees F.*	*Air-fuel ratio*
Part I	2	500	Nil	125	Not controlled (125 app.)	9-1
Part II	2	2,500	45	95	165	14·5-1
Part III	2	2,500	45	200	245	14·5-1

Initial oil fill 7½ lb
Oil make up Every 12 hours

TABLE V

LAUSON CW PROCEDURE A

Engine .. .. Lauson H2
Operating time (total) .. .. 90 or 120 hours

Details of cycle	*Time, min.*	*Speed, revs/min*	*Load, b.h.p.*	*Coolant outlet temp., degrees F.*	*Sump oil temp., degrees F.*
Condition A	15	700	Idle	Not controlled	Not controlled*
Condition B	6	2,400	4·0	60/65	70/90

The engine is run in 10-hour periods with conditions A and B alternating as shown. Rings are weighed every 30 hours.
Initial oil fill .... 2 lb
Oil make up .. .. .. Every 10 hours
**Note:* Temperatures settle a few degrees below those at Condition B.

the aqueous corrosive media from making contact with the metal surfaces. In addition, cold starting requires a rich fuel/air ratio, giving sooty combustion. The cold aluminium piston is not as big as it ought to be under running conditions, so there is blow-by, and thus cold sludge is found in the cooler parts of the engine. This is the black mayonnaise type of water-in-oil emulsion. It may be clean water and clean oil, forming a water-in-oil emulsion stabilized by soot from the combustion.

A great deal of research has been put into the problem of controlling low-temperature cylinder wear and formation of cold sludge. Again, engine tests are necessary, and a great variety have been devised. Much co-operative work has been done in the United States on low-temperature operation of engine tests. The FL-2 procedure (TABLE III) is now some years old, but the test is largely discredited for evaluating lubricants. It is said to be good for

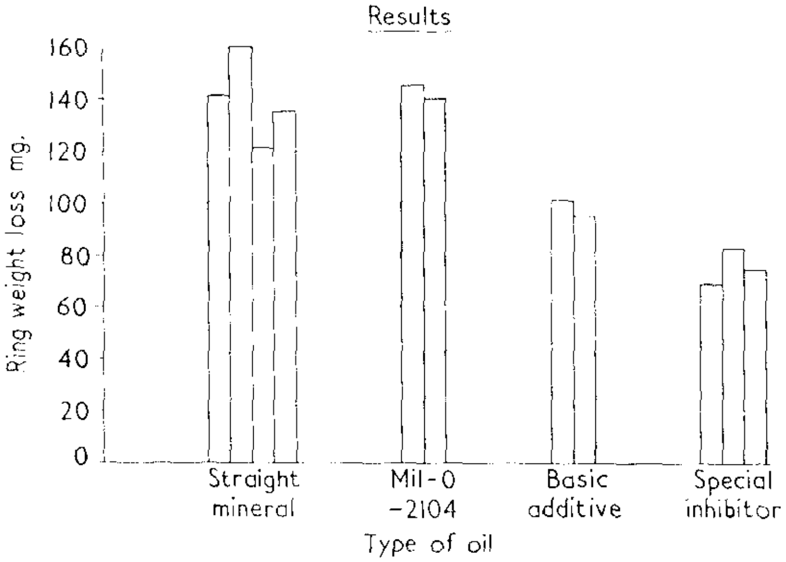

FIG. 1

evaluating the dirtiness of fuels in low temperature operating conditions.

The Ex-2 procedure (TABLE IV) was co-operatively developed in the United States to try and overcome the disadvantages of the FL-2. Certain modifications were made to the engine ; rocker-cover vents welded shut, to reduce the ventilation and give more chance for water condensation to produce cold sludge ; vertical notches in the compression rings to permit more blow-by ; and a cycling load and speed procedure was used. It was not successful and the Co-operative Lubricants Research Committee went to work again, and are now devising an Ex-3 procedure. These things show how difficult is the problem of evaluating oils and additives to cope with the difficult low temperature conditions.

In addition to those two American projects, there have been some efforts made in the United Kingdom, where a little single-cylinder Lauson engine was used, instead of a 6-cylinder Chevrolet, and the Lauson CW procedure was devised (TABLE V). It is a cycling procedure, with low speed, followed by high speed with a very low coolant temperature.

FIG. 1 shows the effect of additives on piston ring weight loss, a measure of low temperature wear in that procedure. There is a very high weight loss with the straight mineral oil ; the ML-2104 oil is not much better. The basic additive effects some improvement, and a special basic additive is a little better still.

FIG. 2 reveals ring wear in mg/hr from a large number of tests. These are averages, and they show the evil effect of low jacket temperature, and the very good effect of high jacket temperature. It is seen that between 2½ and 6 mg/hr can be lost off the piston rings with a 60 degrees F. jacket temperature, down to almost nothing at 350 degrees F. What the lubricant is bothered with is cold, not heat.

In this 60 degrees jacket temperature series of tests, a peculiar effect was found—that is, piston skirt corrosion. FIG. 3 shows a corroded piston from that low-temperature work, and a similar piston using an additive in an attempt to combat that effect. As is usually the case with tests when using accelerated conditions to try to get results quickly, peculiar effects arise. This corroded piston effect has been seen about three times in the last thirty years from vehicles in service, so its incidence is entirely negligible. However, it is found every time with straight mineral oil in the Lauson test, with the jacket temperature

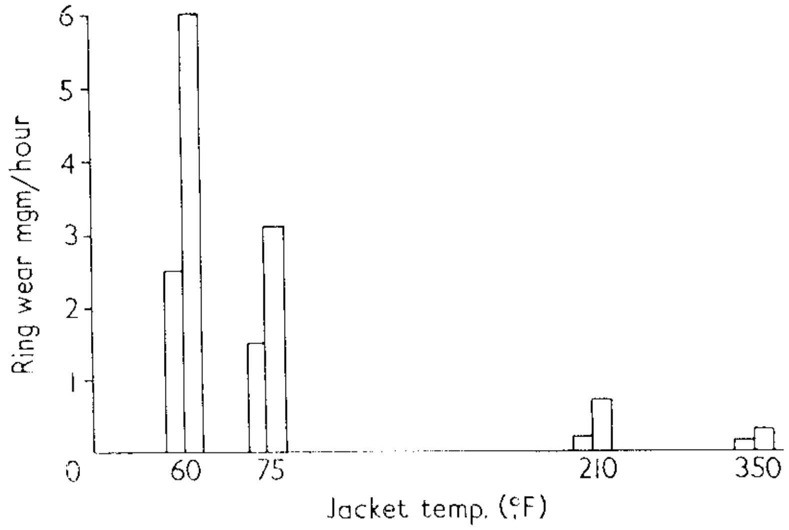

FIG. 2

TABLE VI

AUSTIN AC/8 PROCEDURE

Engine . . . . Austin
Modifications to engine:
1. Compression ring gaps increased to 0·030 in.
2. Oversize idling jet fitted to give rich mixture.
Actual operating time (total) 153 hours (17 cycles)

Details of cycle	*Time, hours*	*Speed, revs/min*	*Load, b.h.p.*	*Coolant outlet temp., degrees F.*	*Oil temp., degrees F.*	*Sump Cooling Fan*
Condition A	1	750	Idle	90-95	Not controlled (90 app.)	Full on
Condition B	1	2,000	10	125 ± 2	160 ± 2	As required
Condition C	1	Shut down		Coolant circulating		Full on

A complete cycle consists of 9 hours running alternately at conditions A and B followed by 1 hour at condition C thus:—
ABABABABC

Initial oil fill . . . . . . 6¾ lb
Oil make up . . . . . . Every complete cycle

TABLE VII

LOW TEMPERATURE WEAR AND SLUDGE TESTS
AUSTIN AC/8 PROCEDURE. 17 CYCLES
Total 156 hours

	Reference oil ET/137/55 Anti-oxidant mildly detergent	*Special oil ET/9/56 Anti-oxidant Anti-corrosive*
Total sludge rating max. 60	33·9	35·8
Mean max. wear all bores—10-4 in. . .	3·9	0·8

FIG. 3

at about 60 degrees F. The question is whether the conditions have been accelerated by this cold jacket so much that the test is no longer of value.

Not being entirely satisfied with the Lauson results mentioned, a procedure (TABLE VI) was devised with a 10 h.p. Austin engine. The ring gaps were increased, an oversized jet fitted to give rich mixture, and a cycling procedure using low speed-low load and high speed-high load, followed every nine hours by one shut down with the cold water circulating to get static condensation in the engine. Some results were obtained from those tests (TABLE VII), but they did not tell a great deal about sludge.

However, it can be seen that it is possible to bring down the rate of bore wear very considerably and to get nearly two more marks in the matter of sludge, which is a great help.

As has been said, a great deal of work is going on in the United States and Europe to find the answers to the evil effects of low temperature operation, and this is particularly important in the United States because the competitive state of their motor manufacturing industry causes them to build bigger and bigger engines of higher and higher horse-power, which they cannot use. The consequence is that 90 per cent of U.S. cars may be operating at the highest speed that the road conditions will permit, but the engines are only idling, so the evils of low temperature operation are with them much more than they are in the United Kingdom with its smaller high revving engines.

However, results are being reported from all this work, and new organic compounds containing phosphorus and sulphur have given promising results, and good performance has been reported on nitrogen-containing polymers, alkyl amino alkyl methacrylates which combine viscosity index improving and sludge dispersant properties.

The Patent literature has recently mentioned a co-polymer of dodecyl methacrylate and ethanolamine methacrylate, a co-polymer of alpha octadecene and acrylonitrile and a tri-polymer of palm kernel fumarate vinyl acetate and acrylonitrile. There is much activity in this field !

Viscosity Index Improvers

All oils become thicker when cooled, and thinner when hot. But the difficulty can be alleviated by the use of viscosity index improvers, which are all polymers

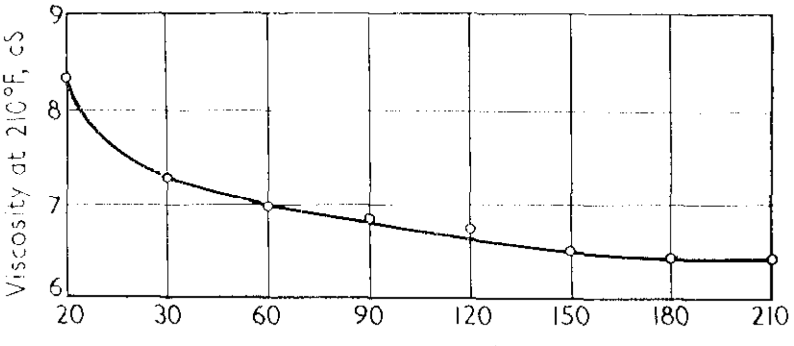

FIG. 4

from either isobutene, methacrylate esters, or styrene. They are not readily soluble in cold oil, and apparently exist therein in a kind of colloidal suspension with the long chain polymer curled up, but when the oil is heated the long chain polymer straightens out and goes into complete solution, whereby it has a substantially greater thickening effect on the oil, and thus the viscosity index is improved.

With these polymeric viscosity index improvers, it is possible to make multigrade oils. Great advantages are claimed for these, such as ease of starting when cold, quick circulation of oil from cold start, reduced fuel consumption, lower octane rating requirement increase, and no increase in oil consumption. Those are the claims, and to a considerable extent, well-founded, although it must not be thought, of course, that large-scale use of viscosity index improvers will solve all these problems. The ease of starting from cold, the quick circulation from a cold start, and the reduced fuel consumption, all depend upon low viscosity at cold starting temperatures. The ASTM Handbook recommends that the viscosity at low temperatures should be ascertained by extrapolation on the ASTM Viscosity Temperature Chart from viscosities determined at, usually, 100 degrees and 210 degrees F. The ASTM Viscosity Temperature Chart is all very well for Newtonian fluids, but oils containing viscosity index improvers cease to be Newtonian fluids at temperatures of the order of 40, 50 or 60 degrees F. and if the viscosity at 32 degrees F. or zero is required, extrapolation on the ASTM Chart is probably quite misleading. The true viscosity of the oil at those low temperatures will be higher than the extrapolation indicates.

The actual determined viscosity at low temperature depends on the rate of shear in the instrument used for the viscosity determination, but only at the very high rates of shear will the true viscosity coincide with that on the extrapolated curve. This is a very complex subject, and it has been discussed at length in the relevant literature, with widely divergent views from the experts on both sides.

The viscosities of oils containing viscosity index improvers are, as has been said, reduced by shearing stresses. Viscosity index improvers vary in their shear stability, and it is important to ensure that the finished oil will not suffer an unacceptable loss of viscosity under the shearing stresses imposed in service. Shear stability depends on molecular weight and structure of the polymer, and its concentration. In general, the higher the molecular weight, the lower the shear stability.

It is not easy to measure shear stability accurately. One method which is reasonably useful measures loss of viscosity due to cycling the oil through a Diesel fuel injector nozzle. More recently, ultrasonic vibration in sonic oscillators has given promising results, with much reduced time taken for testing.

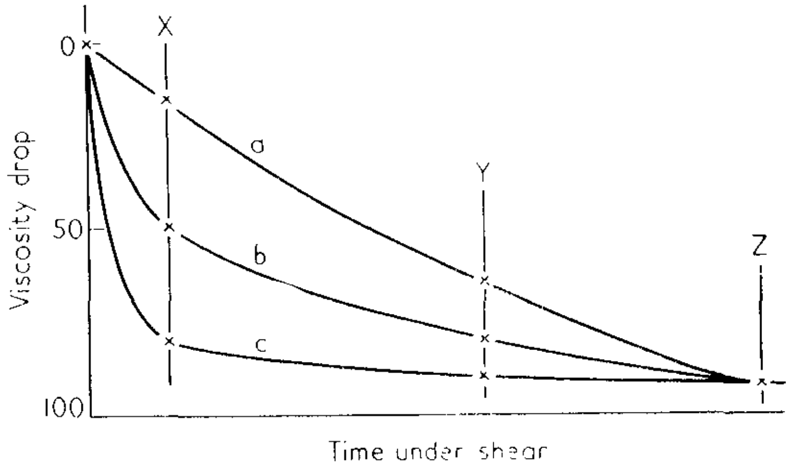

FIG. 5

FIG. 4 indicates the effect of shear upon viscosity. It is clear that the viscosity falls off fairly rapidly with increasing numbers of cycles through the shearing equipment.

FIG. 5 shows theoretical curves to illustrate some of the difficulties of evaluating shear stability from the practical and economic points of view. Curve ' a ' represents an oil containing a viscosity index improver of fairly low m.w., ' c ' represents an oil containing a high m.w. polymer, and ' b ' a type intermediate between ' a ' and ' c '. *How long should the shear test be run ?* If stopped at the point ' x ', oil ' a ' is infinitely better than oils ' b ' and ' c ', but if continued to point ' z ' all are approximately equal. The answer is to run the oils in representative engines, preferably driven by a motor to avoid fuel dilution and oil oxidation effects. After a period representing a suitable road mileage, the practical effect of engine shearing stresses on viscosity can be determined.

Lower octane rating requirement increase may require a little explanation. The car manufacturer wishes to design his engine with a compression ratio as high as the octane rating of the available petrol will allow, but the tendency towards pinking, and therefore the octane rating requirement, increases during the first few thousand miles of driving because of formation of deposits in the combustion chamber. Low viscosity solvent refined neutral oils thickened with suitable polymers, which raise both viscosity and viscosity index, have less tendency to formation of deposits on piston heads and cylinder heads than similar oils thickened with bright stocks. Therefore, they have an advantage from the point of octane rating requirement increase. But it is not an unmixed blessing, because some, at least, of these polymeric thickeners give rise to *increased piston ring groove deposits, especially in compression ignition* engines, and much larger amounts of detergent additives have to be used to control this effect.

No increase in oil consumption is a controversial claim, and it has been discussed from all sides by the experts. Much more study of this subject is needed, but oil consumption is influenced by so many variables that the most careful analysis of results from engines is required before valid conclusions can be drawn. One thing is certain, and that is the higher the concentration of viscosity index improver, the lower the viscosity of the base oil, and the lower the viscosity of the base oil the higher the volatility, and that may become an adverse factor in oil consumption, when high temperature operation is considered.

Pour Point Depressants

These have been known and widely used for many years ; many compounds have been patented, but the types most commonly used are paraffin wax aromatic condensation products, or polymerized methacrylate esters. They appear to have the property of coating the wax crystals and preventing their coalescence as they begin to separate from the cooled oil, so instead of a matrix of interlocking needle-shaped crystals, there are small non-adherent particles of wax suspended in the fluid oil. The reduced pour point obtained by the use of pour point depressants is not necessarily stable in certain conditions of cyclic temperature change, and in some cases the pour point may revert nearly to that of the untreated oil in such conditions. But in recent years pour point depressants have been vastly improved in respect of their ability to prevent pour point reversion, and refiners have contributed by more efficient dewaxing.

Extreme Pressure Additives

Extreme pressure additives are used to increase the load-carrying capacities of oils. The expression EP (extreme pressure) which has become very common, is best reserved for those chemically-active load-carrying additives which are serviceable in hypoid gear oils. A variety of other load-carrying additives, of less activity, but great value in certain applications, are better described as load-carrying additives, the reason being that when people in the industry think of EP additives, they think of the chemically-active hypoid type. In the hypoid gear, a combination of high running speed and high unit loading provides very difficult lubricating conditions, especially during the running-in period. The lubrication requirements are different in low speed-high torque conditions from those in high speed-low torque conditions, and in the past different types of additives have been needed to satisfy either completely. With difficulty a compromise was reached which adequately served both cases, although in certain passenger cars, high speed shock loading conditions required a degree of chemical activity in the axle oil which made it impossible, with the same oil, to satisfy the requirements for low speed-high torque conditions in other vehicles. This goes back to the time when the low speed-high torque kind of oil was required for trucks, and the high speed-low torque shock loading type for passenger cars. A compromise was reached whereby what was called the universal hypoid gear lubricant could be used in both type of vehicles, until the passenger car conditions were intensified to the state where, in certain models, it was necessary to use a higher degree of chemical activity which prevented the oil passing the low speed-high torque test. Compounds of sulphur, chlorine, and phosphorus were generally used, and the mechanism appears to be that the compounds in oil solution are stable at normal bulk oil working temperature, but when minute asperities on the mating surfaces are breaking through the oil film, a rapid temperature rise occurs, and welding of the high spots will take place if no additive is present. Suitable sulphur compounds decompose at the minute points of contact before welding temperature is reached, thus a sulphide film of lower melting point than the metal is formed, and welding is prevented. Chlorine compounds act similarly by the formation of chloride films. Therefore, the effectiveness of an additive under any given condition probably depends on the temperature at which it will react with the metal of the gear, and the nature of the film so produced. Iron sulphide films provide the best resistance to welding, and are stable at high temperatures, over 800 degrees C., but they have a high co-efficient of friction. Iron chloride films have a lower co-efficient of friction, but break down at about 300 degrees C. Phosphide films, which are believed to form a low melting eutectic with the free metal, are probably formed by compounds containing trivalent phosphorus at moderate temperatures, and provide protection against metal deformation under conditions of low speed and high torque.

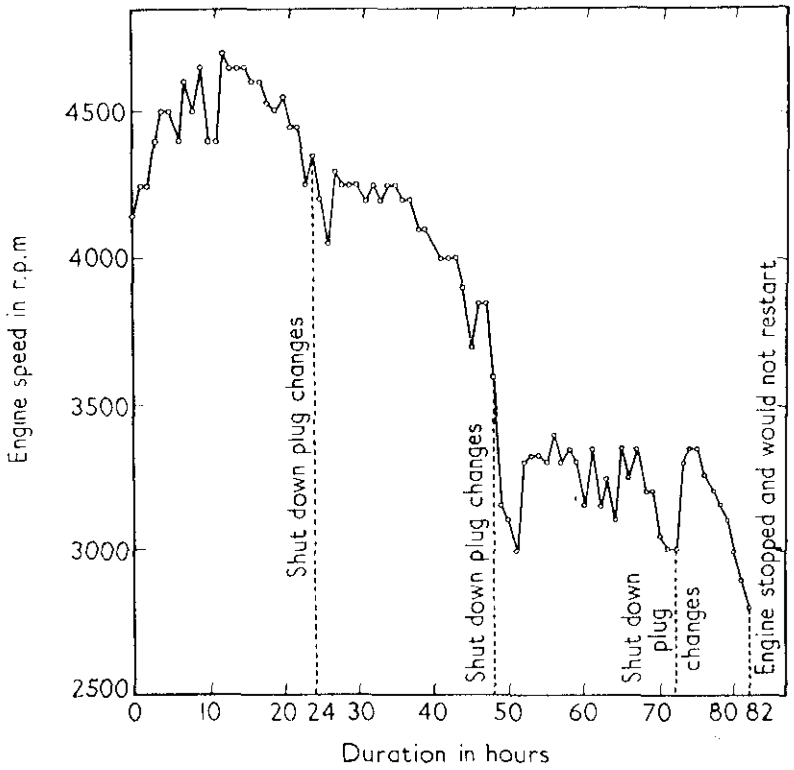

FIG. 6

Two-Stroke Engines

Two-stroke engines are now very popular ; their numbers are increasing every day. They have a great variety of designs, and quite a big oil consumption; their little engines use about as much oil as a 10 h.p. car, so that they ought not to be neglected. They have various troubles—port blocking and exhaust system blocking ; carbonaceous deposits in the combustion chamber ; failure of crankshaft ball-bearings by wear or corrosion ; spark plug bridging ; and piston ring sticking and piston seizures, due to metallic contact or the filling up of the clearance with lacquer.

It is very difficult to get any sense out of two-stroke testing. These engines are very variable in their behaviour. In some engines, high viscosity index solvent-extracted oils give better results than medium viscosity index naphthenic type oils, and in other engines, the reverse is the case. Using the same engine, the oil results can be reversed by changing the conditions of test. If oils do produce port deposits, it is desirable that they form deposits of the type which break away before becoming so great as to reduce engine performance.

FIG. 6 shows the reduction in engine speed due to blocking of the exhaust port, reducing the efficiency of the engine. The occasional increase in speed are due to the breakaway of deposits improving performance for a short time.

FIG. 7 is the result of photographing the exhaust port at intervals during the running of a two-stroke engine on the road. The percentage of exhaust port area blocked increases to between 40 and 50 per cent ; thereafter it fluctuates within these limits by build-up and breakaway of carbonaceous deposit. Incidentally, this performance has been repeated entirely, and it gives an almost identical curve. It is a delightful piece of repeatability from a road test and is the sort of thing which is rarely experienced.

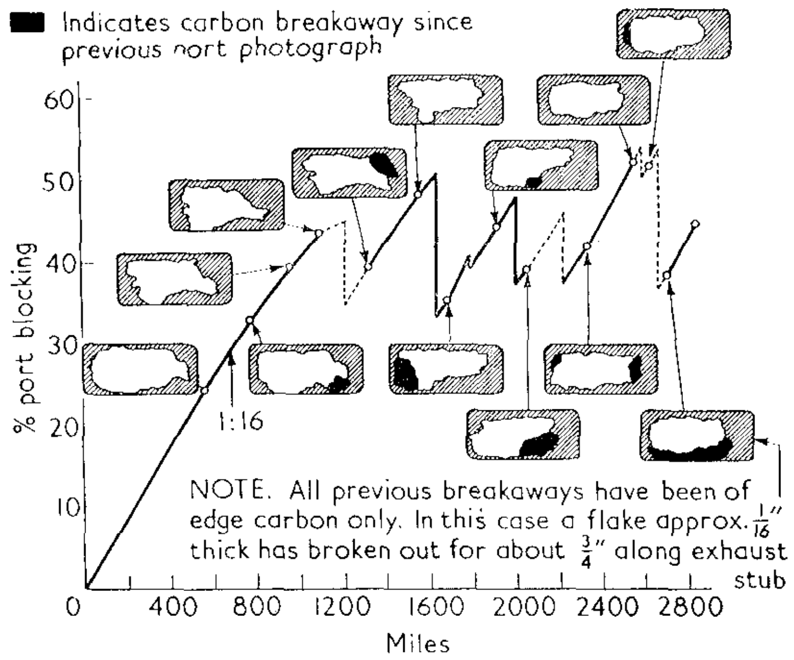

FIG. 7

Steam Turbine Additives

Various additives improve the performance of steam turbine oils. A comparatively recent development in the field of load-carrying additives is the production of steam turbine oils having superior load-carrying properties to protect highly stressed marine turbine reduction gearing. Additives for this purpose must be selected with great care, for the essential properties of steam turbine oils—oxidation stability, good demulsification value, and ability to prevent rusting in the presence of sea-water—must not be impaired. The increase in load-carrying capacity which can be achieved is shown in TABLE VIII.

This development enables the gear designer to design smaller and lighter reduction gearing of higher unit loading and higher sliding speeds without risk of scuffing.

Oxidation and Rust Inhibitors for Steam Turbine Oils

It is convenient at this point to mention other additives used in steam turbine oils, more particularly oxidation inhibitors and rust inhibitors. The amines and phenolic compounds find their application here and by careful selection of stable base oil and suitable oxidation inhibitor, steam turbine oils are being made in the confident belief that the oil will never need to be discarded during the whole life of the turbine.

Water is often present in the lubrication systems of steam turbines. Good turbine oils, designed to separate water quickly do not readily wet metal surfaces. Iron surfaces in the system can be wetted by water, causing rusting, and rust is a good stabilizer of water-in-oil emulsions. Certain surface active agents, introduced into steam turbine oils in very small proportions, have a quite remarkable effect in preventing rusting of the ferrous parts of the oil system, even in the presence of sea water. The mechanism by which these inhibitors act is interesting. They become absorbed on the metal surfaces, forming a barrier to the water and oxygen which cause corrosion. Thus they leave the oil, in which they were introduced to the machine, with the result that a sample

TABLE VIII

Oil	*Scuffing load, lb at 70 degrees C. IAE gear test rig*			*Full-scale marine gearing of advanced design*
	2,000 *revs/min*	4,000 *revs/min*	6,000 *revs/min*	
Regular marine turbine oil A	60	40	25	Scuffed at 65 per cent full power torque
Oil A + load-carrying additives	125	105	100	No scuffing at 130 per cent full power torque

of oil drawn from the turbine may give a bad result on a laboratory rusting test, yet the turbine is free from rusting because the inhibitor has ' plated out ' on the metal surfaces where it remains quietly doing its work.

Additives for Marine Diesel Engine Lubrication

In the smaller, high-speed, trunk piston engines, conventional heavy-duty oils containing anti-oxidant and detergent additives, are quite successful in keeping engines clean and piston rings free, and extending overhaul periods. Different conditions prevail in the large, slow-moving crosshead engines where the cylinders are lubricated by a mechanical lubricator. In the crankcase oils for these engines, anti-oxidants, in some cases of the turbine oil type, have given good results. Where corrosive combustion products have access to the crankcase oil, pitting of crankshaft journals is sometimes a problem which can be alleviated by the use of oil soluble compounds of basic properties to neutralize the acidic products of combustion.

In the large cylinders, especially when high viscosity, high sulphur content, boiler fuel is used, combustion chamber fouling and high rates of liner wear are experienced. The conventional detergent additives, even if basic in reaction, are not very successful, apparently because the lubricant is admitted to the cylinders in such small quantities that the amount of additive present is insufficient to cope with the deleterious combustion products. The problem is being tackled in several different ways :

(1) By making the cylinder oil highly alkaline by incorporating a relatively large proportion of strongly basic, oil-soluble organic compounds;

(2) By carrying high basicity into the oil by emulsifying therewith an aqueous solution of oil insoluble, water soluble salt;

(3) By introducing colloidal suspensions of inorganic compounds, e.g. chalk, into the oil.

These methods have shown promise in field service trials, resulting in reduced liner wear and cleaner engines.

Gas Turbine Lubricants

The requirements of aircraft gas turbines in the way of lubricants present an immense field for additives, because they are constantly asking for what appears to be impossible by way of low temperature fluidity, extremely high temperature stability, and high load-carrying capacity. So there is plenty of scope for additives. There are anti-oxidants, load-carrying additives, and possibly detergents to clean up deposits from oils inadequately arranged from the point of view of oxidation resistance. The basis of these lubricants are not conventional hydrocarbons, but usually di-esters of sebacic acid or azaleic

TABLE IX

GAS TURBINE LUBRICANTS

Composition	*Load at incipient seizure kg*	*Weld load kg*	*Wear scar diam. (mm) at load (kg)*		
			50	100	150
Ester + PE 20 . .	85	110	0·32	3·2	—
Ester + PE 12 . .	85	130	0·32	2·5	—
Ester + S4	55	130	0·4	2·5	—
Ester + PE 12 + S4 . .	110	165	0·32	0·4	2·7

acid, and pelargonates. TABLE IX shows Four-ball machine results from esters treated with different additives. It particularly brings out the synergistic effect on load-carrying capacity of having both the phosphate ester (PE 12) and the sulphur compound (S4) together in the synthetic fluid.