PRETREATMENT OF SMALL FOUR-STROKE ENGINE COMPONENTS FOR NO-OIL HOT TESTS

by

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(ABSTRACT)

“Hot-tests” form a vital facet towards the end of the production line of modern automotive plants, where the condition of the engine is checked by running it for a short period of time, to ensure its performance under standard operating conditions. The duration of hot-tests for small engines varies from 20-75 seconds.

In the conventional procedure, about 10-30 grams of lubricant (for pre-coating) is used with about 650ml of standard oil for engine testing. However, about 1-3 oz. of oil is lost per engine, as it cannot be sucked out of the crankcase after the hot tests. The loss of 1-3 oz. of oil leads to a significant loss in revenue, over the large number of engines manufactured. It also causes a potential safety and environmental hazard due to leakage of lubricant during shipping or upon first use in a particular application. The goal of this project is to conduct “no-oil” hot tests using less than 10 grams of specially formulated lubricants for pretreatment. Implementation of this procedure for conducting the hot tests in the manufacturing facility would save revenue and eliminate potential hazards mentioned above in addition to cutting down on manpower and/or machinery used for handling the engine oil.

An experimental study of pre-treatment of interacting interfaces of engine components, with specially formulated lubricants, for no-oil hot tests is presented. This study includes sixteen tests performed on the production line of Tecumseh's small engine manufacturing plant. The formulated lubricants were made up of tribopolymer formers, i.e., monomers, which were used in previous tribopolymerization studies. Tribopolymerization is defined as the planned or intentional formation of protective polymeric films directly and continuously on rubbing surfaces to reduce damage and wear by the use of minor concentrations of selected compounds capable of forming polymeric films *in situ*.

This study entailed the investigation of the anti-wear properties of the formulated lubricants on a high temperature pin-on-disk machine and subsequent selection of lubricants exhibiting superior performance for use in the engine tests. The no-oil hot-tests performed at Virginia Tech and on the assembly line exhibited the superior anti-scuffing/anti-wear properties of the specially formulated lubricants, to warrant their use on the production line in the near future.

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CHAPTER 1

INTRODUCTION

Tribology, defined as "the science and technology of interacting surfaces in relative motion and of related subjects and practices", has its origin in the Greek word "tribos", meaning rubbing. This vital element of engineering encompasses a multitude of subjects including the fields of friction, wear and lubrication.

Tribology is thus a study of the friction, wear and lubrication of engineering surfaces with a view to understanding surface interactions in detail and then prescribing improvements in given applications. Its study is crucial to attaining a better understanding of all systems, dynamic or otherwise. Advances in this truly interdisciplinary field have brought about an increase in equipment lifetime and reliability; they have also have decreased energy requirements and downtime of dynamic machinery. The practical importance of tribology is perceptible today, even to the layman.

1.1 Project Significance and Rationale

Internal Combustion Engines date back to 1876 when the first four-cycle spark ignition engine was developed by Otto. This engine had a thermal efficiency of only 11%. There has been an increasing demand, ever since, for new types of I. C. Engines with high work output, higher efficiency, better specific fuel consumption (sfc), longer engine life and environmentally safe emissions. Considerable progress has been made in this regard by reducing friction and/or wear, by proper lubrication and by the use of better additives.

The small engines are omnipresent and are versatile with respect to their end use. Some applications include hand-held power tools, water transport (outboard motors), generating sets, snow blowers, lawn mowers and motorbikes. Moreover, power tools and equipment using small internal combustion engines have become commonplace over the past few decades. The four-stroke engine is unique in several aspects when compared to its two-stroke counterpart. The engine mechanism is more complex due to several moving parts and the work output per engine size is also low. However, these factors and the higher initial cost are offset by the higher volumetric, thermal and part load efficiency, lesser cooling and lubrication requirements and lower rate of wear and tear (at least at the piston-cylinder interface in comparison with the two-stroke engine). Hence, the majority of all reciprocating engines operate on this cycle [1].

1.1.1 Hot tests

A crucial phase at the end of the assembly process in all modern automotive engine plants consists of the so-called "hot tests" [2]. The hot tests are primarily conducted to check the condition of the engine; their duration varies from 20-75 seconds for small engines. The conditions existing during this stage is not the same as that existing during normal operation of the automotive engine. This phase initiates a unique process called "running-in" and also starts the stabilization of the tribological parameters at their optimum level.

Running-in was defined by Summers-Smith [3] as "the improvement of surfaces by removal of high points to make them better able to accommodate a fluid film". Perhaps, the relevance of these hot tests can be better understood by the statement of Gumbleton [4] that in an I.C. engine, 75% of the total wear which took place during a 2 hour run occurred in the first 6 minutes.

On the production line of small four-stroke engines, it is customary to pre-coat important parts such as piston-piston rings, cylinder, cams, cam shaft bearings etc. with special oils and greases prior to assembly before carrying out the hot tests. These tests are then carried out using the normal charge of oil in the crankcase [5]. Some engine plants, which are not totally automated, employ personnel to pour the requisite amount of oil into the crankcase and to drain it out with a suction device after the test is over. However, some oil may remain in the engine after a hot test. This represents a significant loss in revenue since a large number of engines are involved. For example, every 60 ml of oil left behind in an engine after the hot tests leads to a loss of about 6.34 cents per engine (at the market rate of $1.00 for one quart of 5W30 multi-grade oil) or about $250,000/year for 4 million engines. It also causes a potential safety and environmental hazard due to leakage of lubricant during shipping or upon first use in a particular application [5].

The conventional procedure may use about 10-30 grams of lubricant (for pre-coating) with about 650 ml of standard oil for engine testing with a net loss of about 30-90 ml of oil in the engine after the hot tests. The goal of this project is to conduct “no-oil” hot tests using less than 10 grams of specially formulated lubricants for pretreatment. Implementation of this procedure for conducting the hot tests in the manufacturing facility would save revenue and eliminate potential hazards mentioned above. Also, cutting down on manpower and/or machinery used for handling the engine oil saves time and money.

1.2 Objectives of this Research

The concept of tribopolymerization as a potent mechanism of boundary lubrication offers a possible mode to decrease lubricant utilization during hot tests, substantially. Tribopolymerization is described as the planned and intentional formation of protective polymeric films directly and continuously on surfaces in tribological contact to reduce damage and wear [6,7]. This concept is discussed in detail in the succeeding chapter.

The anti-wear compounds developed from this technology are effective with metals, alloys and ceramics, both in liquid and vapor phases. The primary objectives of this study are outlined below.

1. Development of an inexpensive experimental set-up to carry out no-oil hot tests in the I. C. engine lab of Virginia Tech, using small four-stroke engines (No-oil hot tests refer to the condition wherein no lubricant is contained in the crankcase. However, pretreatment of interacting interfaces is done using a small amount of lubricant).
2. Development of a test procedure that matches or exceeds the severity of conditions existing on the production line for conducting the hot tests.
3. Evaluation of the anti-wear and anti-scuffing performance of compounds developed from the technology of tribopolymerization, through their direct use as a pretreatment of engine components, in four-stroke engine tests.
4. Investigation of the occurrence of tribopolymerization at different interfaces in the four-stroke engine that were pretreated by the anti-wear/anti-scuffing compounds.
5. Investigation of the anti-wear properties of compounds/lubricants on a high temperature pin-on-disk machine and subsequent

selection of compounds exhibiting superior performance for use in the engine tests.

6. Determination of the possible correlation of the results achieved on the pin-on-disk machine to their effectiveness in engine tests.
7. Formulation of lubricants that render exceptional anti-wear characteristics and meet the requirements of viscosity, fluidity to enable their use on the production line without changing the current equipment or the procedure.
8. Eventual implementation of an effective no-oil hot test procedure on the production line of 4-stroke engine manufacturing plants.

These objectives include two separate, parallel entities of experimental work that eventually complemented one another: the engine tests and the work on a high temperature pin-on-disk machine. The respective results are presented separately but are correlated and discussed together in the concluding chapters.

CHAPTER 2

LITERATURE REVIEW

This chapter deals with the study of the different facets that make up this research. Beginning with a review of the different systems and components that make up the four-stroke spark ignition engine, ‘running-in’ of engine components and the factors affecting the same are analyzed along with a thorough analysis of the concept and applications of ‘tribopolymerization’.

2.1 The Four-Stroke, Spark Ignition, Internal Combustion Gasoline Engine

2.1.1 Components of a Small Four-Stroke Engine

The components of such an engine are shown in Fig. 2.1 below.

Cylinder Block: The cylinder block is a one-piece die-cast aluminum alloy or cast iron cylinder casting that houses the piston, valves and other internal components within the cylinder cover.

Cylinder Head: A one-piece aluminum alloy or cast iron casting that is bolted to the top of the cylinder block. The fins on the cylinder head dissipate heat and cool the engine.

Piston: The primary component of an IC engine. It takes the fuel mixture through the different strokes and transmits the force of burning and expanding gases through the connecting rod to the crankshaft.

Piston Rings: Provide the seal between the cylinder wall and the piston. The rings keep the combustion gases from entering the crankcase, wipe the oil off the cylinder wall and return it to the sump.

Connecting Rod: The connecting rod assembly is the link between the piston (pin) and the crankshaft.

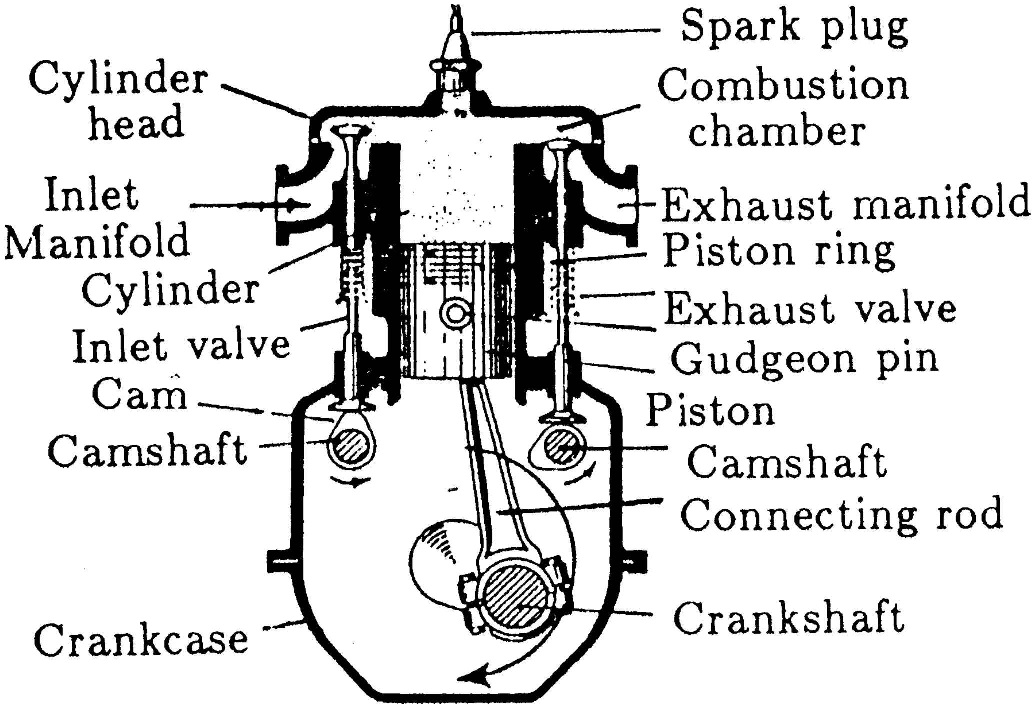


FIGURE 2.1: Components of a Small Four-Stroke Engine

Crankshaft: Converts the reciprocating force of the piston into torque by means of an offset crank pin or rod journal.

Flywheel: Generally made of aluminum alloy or cast iron. Provides the mass to smooth the effects of one power stroke every other crankshaft revolution. The fins on the flywheel act as a fan to cool the engine.

Camshaft: Holds the lobes or cams that control the valves (through valve lifters) to take in the air-fuel mixture and send the combusted gases out of the cylinder. The gear on the camshaft meshes with one on the crankshaft to time the operation of the valves.

Valves: Allow the air-fuel mixture to enter the cylinder and the exhaust gases to exit. The valves provide a positive seal when closed.

Valve Springs: Return the valves to the closed position and maintain valve lifter and cam lobe contact. The valve springs are locked to the valve stem by means of valve retainers.

Valve Lifters: Often referred to as "cam followers." A component in engines that use a linkage system between the cam and the valve it operates. Valve lifters maintain contact with the cams on the camshaft and push the valves open.

Crankcase Breather: It is a one-way check valve that allows air out and prevents air from coming in, thereby developing a partial vacuum in the crankcase during operation.

Cylinder Cover: Provides the bearing surface for the power-take-off (PTO) end of the crankshaft and camshaft. This cover is bolted on and can be removed to provide access to all internal components.

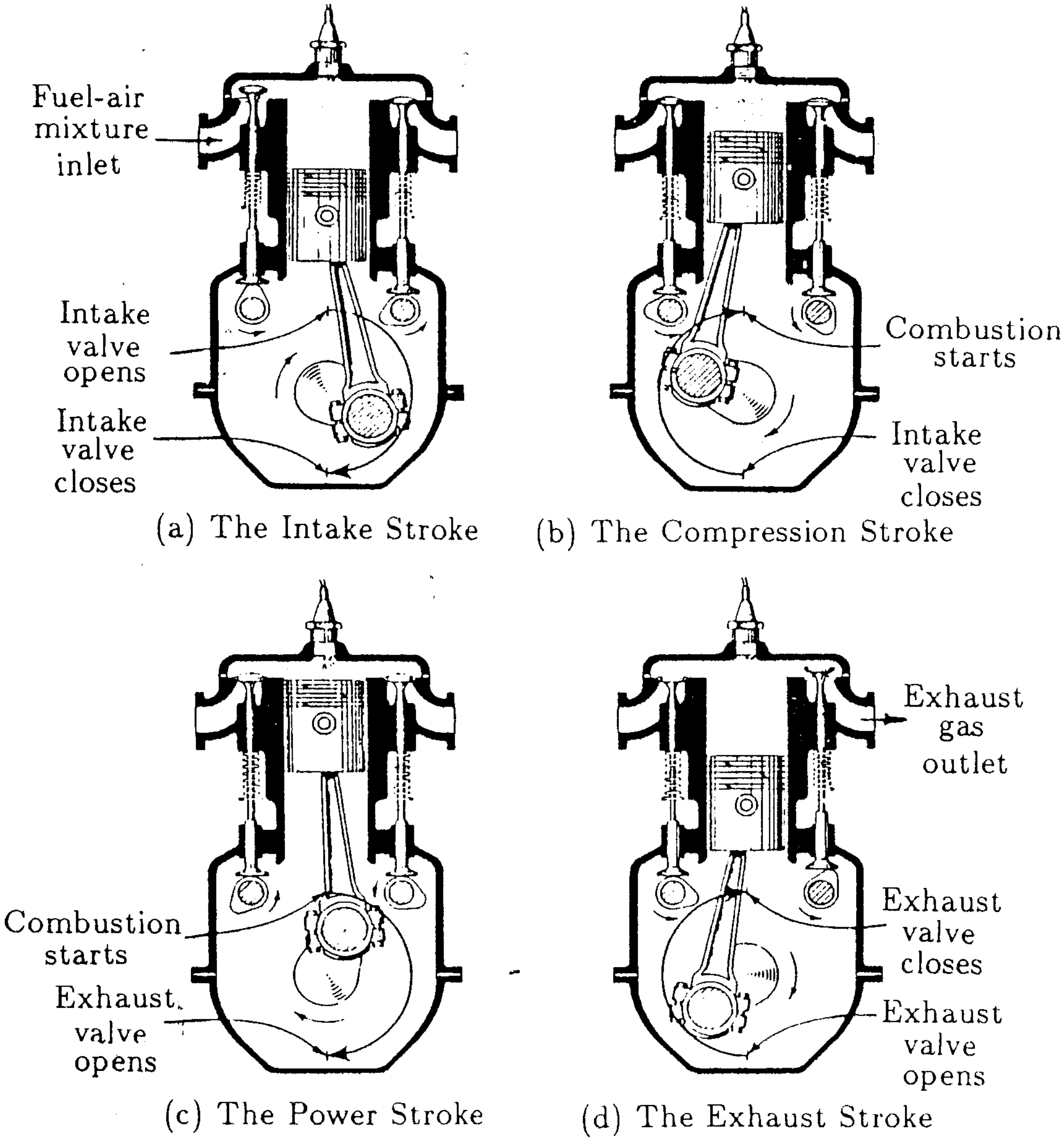
Oil Pump: Used only in vertical shaft engines. Consists of a steel plunger and a nylon housing that rides on the camshaft eccentric.

2.1.2 Operation of a Four-Stroke Engine

In all four-cycle engines, there is one power stroke for every four strokes of the piston. In other words, four piston strokes make up a power cycle. The flywheel on one end of the crankshaft provides the inertia of motion to keep the engine running smoothly between power strokes. The engine camshaft gear is twice as large as the mating gear on the crankshaft to allow proper engine valve timing for reach cycle. The crankshaft makes two revolutions for every camshaft revolution. The different strokes of a four-stroke engine are shown in figure 2.2.

A. **INTAKE**: The intake value is open and the exhaust valve is closed. The piston is traveling downward creating a low-pressure area, drawing the air fuel mixture from the carburetor into the cylinder area above the piston.

B. **COMPRESSION**: As the piston reaches Bottom Dead Center (BDC) the intake valve closes. The piston then rises compressing the air-fuel mixture trapped in the combustion chamber due to both values being closed.



(a) The Intake Stroke (b) The Compression Stroke

(c) The Power Stroke (d) The Exhaust Stroke

FIGURE 2.2: Operation of a Four-Stroke Engine

C. **POWER**: During this piston stroke both the valves remain closed. As the piston reaches the Before Top Dead Center (BTDC) ignition point, the spark plug fires, igniting the air-fuel mixture. In the time it takes to ignite all available fuel, the piston has moved to Top Dead Center (TDC) ready to take the full combustive force of the fuel for maximum power during the piston down.

D.**EXHAUST**: The exhaust valve opens. As the piston starts to the top of the cylinder, the exhaust gases are forced out.

After the piston reaches Top Dead Center (TDC), the four-cycle process begins again as the piston moves downward and the intake valve opens.

2.1.3 Lubrication Systems

Though the description of various systems of a small four-stroke internal combustion engine may not necessary in this chapter, it is helpful to understand the lubrication systems of small engines to better comprehend the selections made for conducting the hot-tests as well as recommendations made for further research.

"Vertical shaft engines generally use a positive displacement plunger oil pump or gear type oil pump. Oil is pumped from the bottom of the crankcase, up through an orifice in the camshaft and over to the top main bearing. Oil under pressure lubricates the top crankshaft main bearing and camshaft upper bearing (Figure 2.3).

The plunger style oil pump is located on an eccentric on the camshaft. As the camshaft rotates, the eccentric moves the barrel back and forth on the plunger forcing oil through the hole in the center of the camshaft. The ball on the end of the plunger is anchored in a recess in the cylinder cover (Figure 2.3). On all Tecumseh vertical shaft four-cycle engines, the oil is sprayed out under pressure through a small hole between the top camshaft and crankshaft bearing to lubricate the piston, connecting rod, and other internal parts" [8] (Figure 2.4). Engine lubrication systems used with most horizontal crankshaft small engines utilize a splash type system. An oil dipper on the connecting rod splashes oil in the crankcase to lubricate all internal moving parts. Some engines have the dipper as an integral part of the connecting rod assembly while others have a dipper that is bolted on with one of the rod bolts (Figure 2.5).

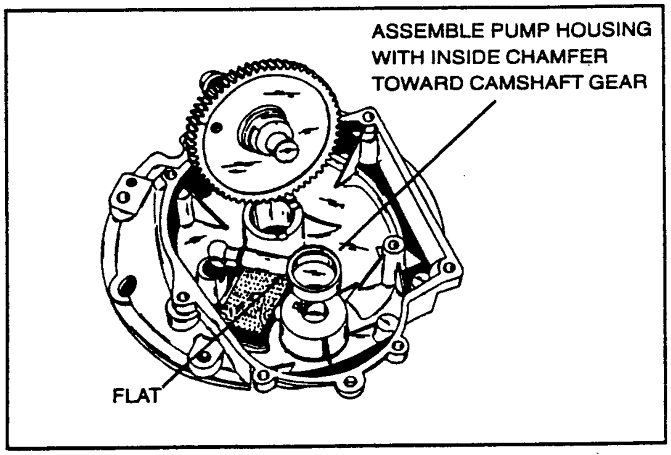


Figure 2.3: Oil Plunger Used in the Lubrication Mechanism of Small Vertical Shaft Engines [8].

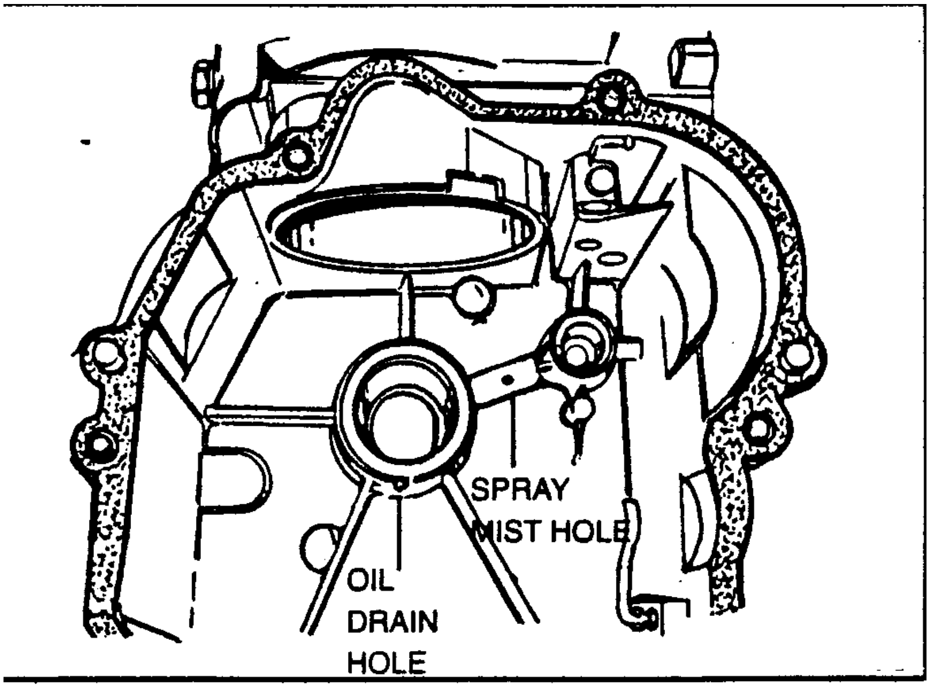


Figure 2.4: Orifices used in the Lubrication Mechanism of Small Vertical Shaft Engines [8].

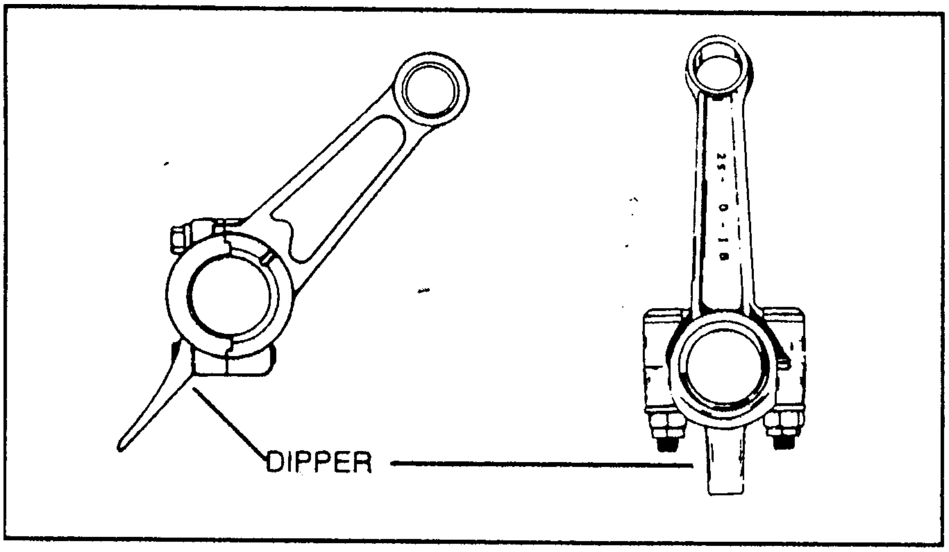


Figure 2.5: Dipper on Connecting Rod – used to lubricate most Small Horizontal Shaft Engines [8]

2.2 Four-Stroke Engine Lubricants

Plain mineral oils have been used in many units and systems for the lubrication of bearings, gears and other mechanisms. Nowadays, however, the requirements are very often greater than what the plain mineral oils can provide and hence, mineral oil in its pure form is seldom used as a lubricant [9,10]. "Almost all commercial lubricants contain additives to enhance their performance in amounts ranging from less than 1% to 25 % or more" [10]. The primary functions of these additives give them their common names listed in table below [9,10].

Table 2.1: Engine Oil Additive Types

Additive type	Function / Working
Anti-wear	Reduce wear / scuffing, prevent seizure. Form thin tenacious films on highly loaded parts to prevent metal to metal contact.
Anti-foam	Suppress the foaming tendency of lubricating oil. Reduces surface tension to speed collapse of foam.
Anti-oxidant	Retard oxidative decomposition. Decompose peroxides and terminate free-radical reactions.
Corrosion and rust inhibitors	Prevent corrosion and rusting of metal parts in contact with the lubricant Preferential adsorption of polar constituent on metal surface to provide protective film, or neutralize corrosive acids
Detergents	Reduce or prevent deposits Chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble.
Dispersants	Keep insoluble contaminants dispersed in the lubricant Contaminants are bonded by polar attraction to dispersant molecules, prevented from agglomerating and kept in suspension due to solubility of dispersant.
Emulsifier	Form a stable mixture, or emulsion, of oil and water.

Extreme Pressure (EP)	Prevents scuffing / seizure of sliding surfaces under extreme pressure conditions
Pour Point Depressant	Reduce pour point to enable flow at lower temperatures. Modify wax crystal formation to reduce interlocking.
Tackiness	Reduce loss of oil by gravity, e.g. from vertical sliding surfaces, or by centrifugal force.
Viscosity Index Improver	Reduce the decrease in viscosity due to increase in temperature.

2.3 Study of running-in, functional properties of a honed surface

Despite an exhaustive literature review, material that indicated prior research in conducting “no-oil” tests or attempts towards *minimalist lubrication* in automotive engines was not found. This resulted in an analysis of existing research material that came closest to the task at hand.

Running-in, also referred to as breaking-in or wearing-in, is the process during which changes in tribological properties occur from start-up to the acquisition of a *steady-state*.

“Steady-state—In tribology, that condition of a given tribosystem in which the average kinetic friction coefficient, wear rate, and / or other specified parameters have reached and maintained a relatively constant level. Note: Other parameters that could be used to define steady state include temperature, concentration of debris particles in a lubricant and surface roughness” [11].

After initial assembly, re-assembly after repair or after periodic maintenance some machines are intentionally subjected to predesigned run-in procedures to condition them for long term operation. In the automotive field, almost all engines go through some form of testing or the other that may either be intentionally designed to bring in certain features by running them in or just to check the conformity of the engine / engine components to certain test parameters (e.g. "hot tests").

A number of articles have been written about running-in and scuffing of engine components but most of them are confined to the piston-cylinder interface and very few deal with the connecting rod – crankshaft bearing interface. As such, the following discussion is about the running-in/scuffing of the piston-cylinder interface.

Murray [12] says that the interest in scuffing at the piston ring-cylinder interface arose due to engine problems both in service as also in manufacturers' "pass off" tests. (The author believes that the term "pass off tests" essentially refers to what we now call "hot tests").

Murray characterized scuffing as "streaks that appear on both rings and bores accompanied by hardened layers which flake off giving rise to high wear rates". Scuffing is brought about by breakdown of the lubricant film supporting the ring surface resulting in high friction, high temperature and local welding of portions of 'interacting surfaces in relative motion'. The prime causes for the breakdown of the lubricant film can be poor surface finish of the bore, wrong design of rings, bore distortion, overheating, too low a lubricant viscosity, ring sticking, inadequate or badly distributed water flow in the cylinder block, deposits packing behind the rings and so on.

Murray also says that though it is more usual for scuffing to occur on the top ring and then to spread down to the second compression ring and the oil control ring, many case histories show that it has started with the second compression ring.

Barber and Ludema [4] and Lansdown [13] say that scuffing in cylinder liners ‘always’ begins at or near the top dead center (TDC) position of the top piston ring. The lubricant temperature at this position (where there is a momentary pause of relative motion) reaches about 200-250°C, evaporating about half of the base oil present in the ring grove. Boundary lubrication takes place at this juncture. Once the oil film becomes too thin to prevent asperity contact, flash temperatures increase the temperature at the contacts leading to local asperity welding, high adhesive friction and area welding and tearing, which, in other words, is called scuffing.

Barber and Ludema mention the scuffing of engine parts is accompanied by the existence of a “white surface layer”. The formation of such a white layer on components in a tribosystem used to *simulate* engine cylinder wear is said to be a stronger criterion to ratify the simulation process than to match other operating conditions of an engine in real time. Though not much is known about this layer it has been speculated to be a result of scuffing and not the cause of scuffing [4].

Lansdown [13] further suggests that prevention of scuffing can be brought about by the use of a suitably curved profile on the piston ring, to ensure adequate oil film thickness. This profile is achieved during running-in, which is "further assisted by the use of specially formulated oil during the first few hours of operation. Another useful technique is the production of a suitable surface texture on the surface of the cylinder liner. Very smooth surfaces tend to increase the incidence of scuffing"[13].

B. G. Rosen et al [14] used the atomic force microscopy (AFM) to study the wear of cylinder bore topography. Their study showed heavy wear at the top dead center and mild wear in the cylinder mid-section. This is in line with statements by Lansdown, Barber and Ludema that scuffing (a form of adhesive wear) begins at or near the TDC.

It is also noteworthy that in a survey carried out by M.J. Neale [15], several diesel engine manufacturers reported an increase in scuffing problems on bringing down the oil consumption level. Also, certain four stroke engines that had just started to scuff, showed signs of scuffing at the top dead center of the cylinder; on certain two stroke engines scuffing was close to the ports. Cylinder bore distortion is another accepted major factor that can stimulate scuffing.

Several papers written in the 1970s mention that engines that have been run-in develop a tapered, double tapered piston ring profile resulting in a barreled type surface [13,16], which aids in controlling throw-off of oil from the piston rings into the exposed combustion chamber [16]. Lansdown [13] (1994) mentions that the development of a suitable curved ring profile is desired and is commonly achieved during running-in and helps in the development of an oil film. However, it is now very common to see this taper incorporated in the design of the piston ring itself.

Scuffing can not be attributed to any single factor and it is influenced by the surface finish of the bore, design of piston rings, bore distortion, ring sticking, surface coatings of piston rings / cylinder bore, viscosity of lubricant, gas pressure variations in the ring pack and so on. It is, however, accepted that machinery is likely to fail early or last a long time [4] and careful selection and controlled operation of break-in procedures are becoming commonplace, by the day, to increase the probability of long engine life.

2.4 The Concept of Tribopolymerization

The concept of tribopolymerization was first conceived by Furey in 1957 [6] and later refined further in collaborative studies between Furey and Kajdas [7, 17]. Tribopolymerization is defined as the planned and continuous formation of protective polymeric films directly on tribological surfaces by the use of minor concentrations of selected monomers capable of forming polymer films “in situ” either by polycondensation or addition polymerization [7].

Tribopolymerization is based on the concept that potential polymer forming compounds or monomers, when dissolved or mixed at low concentrations in a carrier fluid (lubricant), polymerize on highly stressed surface regions in relative motion, under loaded contact conditions. The polymerized films are deposited on the surfaces in contact and reduce wear and surface damage by reducing adhesion, contact stresses and lowering surface temperatures. The films thus act to provide boundary lubrication through a deposition process.

Tribopolymerization is influenced by high surface temperatures, catalytic action of freshly exposed surfaces and possibly other effects such as high contact pressures that occur at very localized, highly loaded contact regions. In a dynamic system, the films are continuously being formed and worn away. The wearing away of the protective film increases surface contact and temperatures, which inturn leads to an increase in the rate of film formation and a reduction in surface contact, yet again. Hence tribopolymerization consists of a continuous film formation/removal/replenishment process. An oversimplified view of the process of tribopolymerization is shown in Figure 2.6.

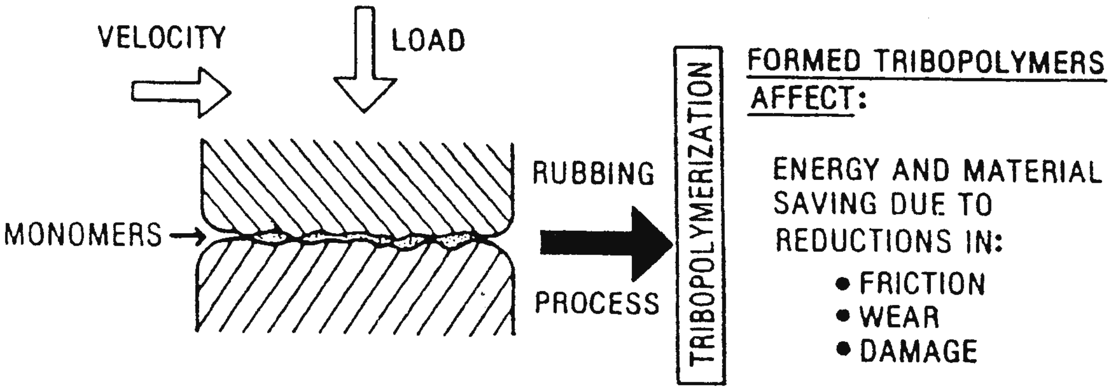
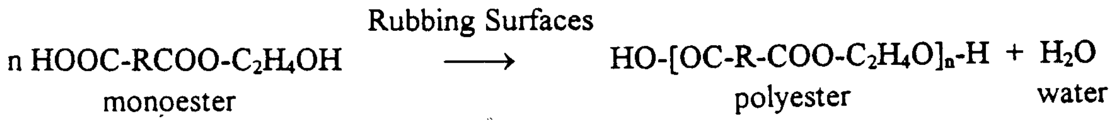


Figure 2.6: Tribopolymerization as a Mechanism of Boundary Lubrication [17]

A large number of monomers were investigated as tribopolymer-forming compounds in Furey's research. An outstanding example of the application of this concept to practical problems was demonstrated by the striking effectiveness of partial (e.g. mono-) esters made by reacting long-chain C_{36} dimer acids with glycols (e.g. ethylene glycol). These compounds were postulated to act by the formation of polyester films as follows:



$$\underset{\text{monoester}}{n\ \mathrm{HOOC\text{-}RCOO\text{-}C_2H_4OH}} \xrightarrow{\text{Rubbing Surfaces}} \underset{\text{polyester}}{\mathrm{HO\text{-}[OC\text{-}R\text{-}COO\text{-}C_2H_4O]_n\text{-}H}} + \underset{\text{water}}{\mathrm{H_2O}}$$

2.5 Applications of Tribopolymerization

Tests carried out by Furey et al. using very low concentrations of certain monomers in hydrocarbon carrier fluids are discussed below. In light of the remarkable performance of these monomers, the concept of tribopolymerization appears to be a potent mechanism of boundary lubrication that offers a mode to decrease lubricant utilization during hot tests, on the assembly line of automotive engine manufacturing plants.

2.6.1 Ryder Gear Tests

The effectiveness of C_{36} dimer acid/ethylene glycol monoester and related potential polymer formers in reducing tribological damage was first demonstrated on a Ryder gear test machine [6]. This is a high load scuffing type test in a complex gear geometry that involves both sliding and rolling contact. The fluid is held in a heated reservoir, usually at 165F, and, sprayed through a jet on the rotating gear surfaces at 270 cc/min with the gears rotating at 10,000 r.p.m. Load is applied for 10-minute periods. The lubricant's ability to resist gear scuffing is evaluated by halting the test after each 10-minute loading periods and examining each of the 28 teeth through a microscope. The test is then resumed at the next higher load step and a curve of scuffed area *versus* load is plotted. The ratings obtained represent the load in pounds per inch of gear tooth width to produce 22½ % scuff area.

Table 2.2. Effect of C_{36} Dimer Acid/Ethylene Glycol Monoester on the Anti-Scuff Properties of Fuels and Lubricants [19]

Base Fluid	**Ryder Gear Scuff Rating (N/cm) on:**	
	Base Fluid	**Base + 0.1% Monoester**
Jet Fuel	700	2600
Turbo Fuel	900	3700
JP-4	350	5200
Xylene	900	6100
Mineral Oil (neutral, 43 SUS/21OF)	2100	4400
Synthetic Oil (C_8-C_{10} Oxo Adipate)	3000	4600

The addition of only 0.1% of the monoester to the four fuel type low viscosity fuels (i.e., jet fuel, turbo fuel, JP-4, and xylene) increased the scuff rating by 1900 to 5200 N/cm (a four-fold to fourteen-fold increase). Moreover, fuels containing monoester as an additive have greater load-carrying capacity than several synthetic and mineral aviation oils [19]. This remarkable performance of the monomer in a variety of hydrocarbon carrier fluids demonstrates its potential to solving poor fuel lubricity problems.

2.6.2 Radioactive valve lifter wear study

A four-stroke, V-8, automotive engine with radioactive valve lifters was also used to study the “in situ” polymer approach to boundary lubrication. 16 radioactive valve lifters were used to study valve train wear in the cam/lifter system under normal operating conditions. During engine operating conditions of no load at constant speed, radioactive valve lifter wear debris would accumulate in the engine crankcase oil. Scintillating radioactive counting techniques were used to calculate the amount of radioactive wear debris in oil samples collected periodically during engine operation. Data obtained during this test is summarized below (table 2.3).

Table 2.3: Relative Additive Wear Protection Using a Radioactive Valve Train Wear Test [6]

Compound in paraffinic mineral oil	**Relative valve lifter wear rate**	**Beneficial carryover effect?**
None	100	------
1% equimolar mixture of C_{36} dimer acid and C_{16} glycol	12	Yes (3-6 h)
1% C_{36} dimer acid	42	No
1% C_{16} glycol	30	No
1% Zinc di(C_6) alkyl dithiophosphate	10	No

It can be seen that the addition of 1% of the C_{36} dimer acid/ethylene glycol monoester to a mineral oil base reduced the rate of wear by over 90%, with pronounced carry-over effects up to 6 hours in a non-additive base oil afterwards. Moreover, this 90%

reduction roughly equals the outstanding effect of zinc dialkyldithiophosphate (ZDDP) additives that are commonly used in automotive engine lubricants, to control valve train wear.

The carry-over effect is important as it demonstrates the formation of a very durable protective film(s) that had formed on the contact region between the valve lifters and the cam. ZDDP, on the other hand, did not show any carry-over effect.

2.6.3 Pin-On-Disk Tests

A series of tests were conducted on a pin-on-disk apparatus to further investigate the effects and potential of tribopolymerization as a mechanism of boundary lubrication. In one study, the apparatus featured a 1/8th inch diameter AISI steel ball sliding against a polished 1045 steel disk [17]. Applied loads ranged from 10 to 30 N for periods of 10, 30 and 60 minutes. A stylus profilometer and photomicrographs were used to measure disk wear. In hexadecane, the monoester reduced disk wear by 95% over hexadecane alone, at 10 N applied load. Significant wear reductions were observed at higher loads although they could not be quantified as a percentage due to excessive scuffing using hexadecane alone. A Fourier Transform Infra Red Microscopy (FTIRM) inspection of the disk samples showed evidence of polymerization (along with other possible chemical reactions) in the wear track but not away from the wear track. Moreover, the quantity of organic material detected in the wear track was at least 25 times greater with the monoester than with dimer acid or a more polymerized diester, by themselves.

Alumina-on-alumina pin-on-disk tests were conducted by Tripathy [20] with selected addition type monomers in a 1% weight mixture in hexadecane. Lauryl methacrylate, diallyl pthlate, vinyl acetate, methyl-2-acrylamido-2-methoxy acetate and vinyl octadecyl ether reduced alumina wear by an average of 63%, 80%, 57%, 56% and 9%, respectively. The poorer performance of vinyl octadecyl ether was attributed to its cationic polymerization mechanism, while the first four monomers can polymerize by either radical or anionic mechanism or both. The addition of any of these monomers in hexadecane did not affect friction significantly. At elevated temperatures of 50-150°C, all the monomers exhibited similar anti-wear characteristics throughout the range, with improvements in some cases.

These pin-on-disk experiments were repeated by Tritt [21] with several monomer additives in hexadecane at higher loads and higher speeds. Tritt found that some of the monomers were extremely effective in reducing wear under low speeds (0.25 m/s sliding speeds) at various loads and ineffective at the highest speed tested (1.0 m/s sliding speed).

2.6.4 Vapor Phase Lubrication

Smith et al. [22], conducted experiments to determine the effects of monomer additives on ceramic wear in the vapor phase, using an inert gas carrier. The liquid additives were heated, vaporized and delivered to an enclosed alumina-on-alumina pin-on-disk contact region by a stream of dry nitrogen gas. Dry nitrogen was chosen, as it is inert to the monomers as well as alumina. The load imposed between the ball and disk was 5 N and the sliding speed was 0.25 m/s. The enclosure was purged with Nitrogen/monomer vapor before each test to eliminate water vapor and gaseous oxygen in order to minimize other undesired reactions.

Three addition type monomers that were tested under a similar geometry and sliding conditions in a hydrocarbon carrier fluid were chosen for the vapor phase study. These monomers were lauryl methacrylate, diallyl phthalate and vinyl octadecyl ether. Worn disk surface profiles were studied and recorded using a profilometer. Selected surfaces were examined using a FTIRM to determine the chemical composition of the surface films left on the wear scar.

Dramatic reductions in ball wear (94-99%) were observed at elevated temperatures. Vapor delivery temperatures were between 120°C to 165°C. With an increase in monomer delivery temperatures, wear reduction capability of the monomers was enhanced. Friction reduction was between 37-50% at the elevated bulk temperature (145°C).

FTIRM surface analysis of the wear scars indicated reactions between the vinyl monomers and alumina. Although, strong evidence of soap formation was found, the reaction mechanism was not properly understood. In the case of diallyl phthalate, strong evidence of surface polymerization was noted. Tribopolymerization could neither be proven nor ruled out for the other two monomers due to poor signal to noise ratios.

2.7 Two-Stroke Engine Work

More recently, Patterson [23] conducted an experimental study of lubrication of a two-stroke engine by tribopolymerization. A condensation monomer (C_{36} dimer acid/ethylene glycol monoester) and an addition monomer (diallyl phthalate) were investigated as potential anti-wear compounds.

The test set-up consisted of a bench on which an air cooled, vertical shaft, Tecumseh TVXL840 two-stroke engine was mounted. The shaft extended through a hole in the bench top and aligned with the axis of a 10 HP AC motor that was bolted to an adjustable mount directly below the engine. A flywheel, installed below the engine gave the system additional rotational inertia. The flywheel prevented the engine speed from dropping below the motor speed during its compression stroke.

A reluctance transducer that was wired to a digital counter provided the engine speed during each test. A thermocouple was used to read temperature of the engine block. The engine speed and temperature were displayed on a computer and the data used to plot temperature *versus* speed graphs.

Measures such as soaking engine components in a naptha solvent bath for 8 hours and cleaning the new piston rings and connecting-rod needle bearings for 15 min. in an ultrasonic bath were taken to remove factory oil films, metal chips etc. from engine parts. The monomers were added to the gasoline as 0.5% (by mass) of the fuel mixture.

After re-assembling the engine with the new piston rings and connecting-rod needle bearings, the engine was subjected to a thirty-minute run-in period that consisted of operating the engine at 2000, 2400 and 3000 rpm for ten minutes each under no load. The engine speed was then dropped below 1800 rpm and the motor turned on, to load the engine. The duration of the engine test was for 20 hours, under mild to severe conditions, to evaluate engine wear and deposit formation. To compensate for shutting down the engine from time to time during the test run, either for re-fueling purposes or for the day, the engine was warmed-up for a period of 10 or 20 minutes, before loading it again.

Post-test disassembly and inspection involved careful visual inspection of each engine part for evidence of deposits, wear debris, surface damage and any other anomalies. Photographs, photomacrographs and SEM photographs were taken of the piston, piston rings and crankshaft surfaces.

Tests were conducted with Diallyl Phthalate (0.5% in fuel), Monoester (0.5% in fuel), Monoester (0.5% in fuel) plus sebacate (0.5% in fuel), Monoester (0.9% in fuel) plus sebacate (0.1% in fuel) and commercial two-stroke engine oil (2.0% in fuel) as the lubricant pre-mixed by mass, in the fuel. A summary of the test results is presented in table 2.4.

Table 2.4: Summary of Two-Stroke Engine Test Results [23]

LUBRICANT (PRE-MIXED IN THE FUEL)	CYLINDER TEMP. AT 2000 RPM (°C)	CYLINDER TEMP. AT 2400 RPM (°C)	CYLINDER TEMP. AT 3000 RPM (°C)	CYLINDER TEMP. AT 1800 RPM LOADED (°C)	COMMENTS
Diallyl Phthalate 0.5%	130	150	210 Failure, 7 min. (Total time: 27 min.)	N/A	- Scuffed piston on major and minor thrust sides - Failed at no-load - Thin yellow-gold and black surface films on the piston - No excessive deposits
Monoester 0.5%	136	170	210	270 Failure, 4.0 min.* (Total time: 34 min.)	*Loaded at WOT - Bottom ring completely stuck - Upper ring stuck 180° -Very viscous, tacky, dark deposits on all lubricated parts - Scuffing on the upper transfer port side of the piston
Monoester 0.5% plus sebacate 0.5%	134	156	212	248 Failure, 3.7 min.** (Total time: 34 min.)	**Loaded at WOT - Both rings completely stuck in piston grooves - Piston Scuffing on major thrust and upper transfer port side of piston - Heavy dark deposits on all lubricated parts
Monoester 0.1% plus sebacate 0.9%	125	143 Test 1 (90 min. no failure)	188 Test 2 (90 min. no failure)	220 Failure, 11 Min*** Test 3 (Total time: 41 min.)	*** Loaded at idle - No evidence of ring sticking - Three narrow scuffed regions on the piston starting at the major thrust side 120° apart - Thin, dark surface films
Two-stroke engine oil 2.0%	130	145	188	238 Failure, at 256**** (Total time: 340 min.)	****Loaded at WOT - Total test time: 340 min. - Significant run-in on piston surface - Sides of piston appear very clean and shiny - One scuffed region on piston: major thrust side

It can be seen that none of the lubricants could prevent engine seizure. With diallyl phthalate as the lubricant, engine seizure occurred even before it was loaded i.e. during the run-in period itself. With monoester by itself and with sebacate as the lubricant, engine seizure occurred immediately upon loading.

It is noteworthy that the commercial two-stroke engine oil at 2.0% in the fuel (which was used as a reference) did not endure the test as well. Therefore, it appears that <u>the operating conditions were more severe than the engine was designed to handle</u>.

At the outset of this four-stroke engine study, this test set-up was evaluated for potential use for loading the four-stroke engines for conducting the hot-tests. Severe vibrational problems were encountered while conducting a test run on a two-stroke engine and the entire test set-up was disassembled to investigate the problem. A one-way clutch that was used in the test set-up (to transfer motion from the engine to the motor and not vice-versa) was found broken. This was caused by the keyway of a coupling into which the one way clutch was shrunk fit. The presence of the keyway in the coupling lead to the roller clutch not being supported all along its outer surface area leading to the protrusion of the clutch into the keyway and breaking up. The use of a coupling without a keyway would have prevented such a breakdown from taking place.

It is a possibility that the clutch might have <u>had broken down towards the end of the very first test that was conducted</u> on the test set-up (using the conventional two-stroke oil as the lubricant @ 2.0%). The non-functioning of the roller clutch would have lead to the motor running the two-stroke engine during the compression / power stroke, when the engine speed could drop below the motor's speed. This could have had induced severe tensions on the engine and could have resulted in early seizure of the same. This theory of the broken roller clutch causing early engine seizure explains the results obtained in the two-stroke engine study where all test lubricants failed in less than 41 minutes.

Moreover, the selection of the test duration, i.e., 20 hours, does not seem to be founded on any solid reason. A reference test conducted on the test set-up using Tecumseh recommended two-stroke lubricant at 2.0% in gasoline failed (engine seizure) after 5 hours and 40 minutes. This is reason enough to repeat the test to get a better idea of the time it takes for seizure to occur using a conventional lubricant. An average of three such reference tests would have given the time it takes to seizure (using conventional lubricants) and this time should have been adopted as the test duration for evaluating the lubricant formulations, tested thereafter. Also, such repetition might have had brought out afflictions (such as the broken roller clutch) in the test set-up prior to the tests using the formulated lubricants.