ABSTRACT

The engine oil lubricates the tribo - surfaces of piston and cylinder of an I. C. engine in liquid state as well as in solid state after burning. The performance of the liquid state is different than the burnt and converted solid counterpart. Oil available as – 20W40, 20W50, 10W30, 15W40, SAE30, 5W30 (sample 1), and 5W30 (sample 2) have given different compositions of residual components which have the properties of solid lubricants.

Keywords: Engine oil, chemical composition. Solid lubricants. Phosphates, sulphates, chlorates, lead.

Introduction:
The engine oil enters in between the tribo pair of piston- cylinder in liquid condition and lubricates the surfaces initially and since the engine oil has lower flash point / fire point than the major constituents of the petrol / fuel, therefore in the engine the atomized oil burns prior to the complete burning of hydrocarbons as fuel. The burnt product of the engine oil then serves as the solid lubricant. The burnt product has the constituents like chlorates, sulphates and other solid lubricants as per the recipe of the engine oil. Thus the engine oil initially serves as liquid lubricant and then as a solid lubricant. Besides this the burnt product of engine oil fills the clearance gap between the piston and the cylinder wall. This makes the piston to move almost linearly inside the cylinder without any piston slap. The filler solid lubricant unfortunately does not have any kind of permanent bonding and remains in its position by the surface roughness of the piston – cylinder tribo pair. Thus the solid lubricant as filler , functions temporarily without permanent sticking and gets detached from the tribo surfaces and gets carried away in to the exhaust. The regular formation and separation of such solid lubricants filling the gap, due to piston movement and taken to exhaust outlet, thus becomes continuous activity. Therefore the continuous replenishment of the engine oil for tribological purpose and its consumption gives the indication of the engine performance. The initial chemical analysis indicates the presence of sulphates, phosphates and lead components.

Chemical analysis:
Test for sulphate (So₄²⁻) and phosphate (PO₄³⁻) radicals-
Sulphate and phosphate radicals are neither acted upon by dil. H₂SO₄ nor conc. H₂SO₄ in cold or warm state. They are identified by individual tests.

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\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}
\] (White ppt.) (Or)

Sulphate (So₄²⁻)
Take solution of mixture in water or HCL or HNO₃ or neutralize Na₂CO₃ extract with dilute HCL and boil to remove CO₂. Add BaCl₂ solution, white precipitate is formed. Decant off and add conc. HCL to the precipitate. It doesn’t dissolve. This confirms the presence of sulphate radicals SO₄²⁻.

On adding BaCl₂ solution to aqueous solution or neutral soda extract of sulphate salt, a white precipitate of BaSO₄ is obtained which is insoluble in conc. HCL.

Fig. 1 Precipitates of lead, sulphate and phosphate.

Fig. 2 Final filter with wattman paper.

Fig. 3 Burn process of substances in platinum vessel at temperature of 700-800°C.
Test separately-
Substance + dil. HCl → Clear Solution → (Na₂CO₃ ext. + dil. HCl) + BaCl₂ → white ppt. (SO₄²⁻ confirmed) → filter → substance on wattsman filter paper burn in platinum vessel 700 – 800°C → Sulphate (SO₄²⁻ obtained)

Calculation-
Mixture= 1.0242gm
Weight of empty platinum vessel= 23.7063gm
Weight of platinum vessel containing SO₄²⁻ = 23.7764
Net weight of SO₄²⁻ = 0.0701gm
% of Sulphate present in Exhaust = (0.0701 x 0.343 x 100)/1.0242 = 2.3476 %

Phosphate (PO₄³⁻)-
Take the mixture, add 2ml conc. HNO₃ and boil to get clear solution (decant if necessary) or acidify 2 ml soda extracted with dilute HNO₃. Add 2ml conc. HNO₃ and 2 ml ammonium molybdate [(NH₄)₂MoO₄] and heat the solution. A canary yellow precipitate of ammoniumphospho-molybdate or colour is obtained. If arsenic radical is present then perform the test of phosphate with the filtrate of second group. i.e. after As⁺Ⅲ is removed, because As⁺Ⅲ also gives this test. If the filtrate shows positive test for phosphate radicals, then only the presence of phosphate is confirmed.

On adding ammonium molybdate and conc. HNO₃ to aqueous solution or soda extract of phosphate salt and heating the contents, a canary yellow precipitate or colour of ammonium phosphomolybdate is obtained.

Na₃PO₄ + 12(NH₄)₂MoO₄ + 24 HNO₃ → (NH₄)₃PO₄.12MoO₄↓ + 3NaNO₂ + 21NH₄NO₂ .12H₂O
(Or)
(Yellow ppt.)

Test separately-
Substance + conc. HNO₃ (nitric acid) + boil, cool + [(NH₄)₂MoO₄] (ammonium molybdate solution) → boil → canary yellow ppt. (PO₄³⁻ confirmed) → filter → substance on wattsman filter paper burn in platinum vessel 700 – 800°C → Phosphate (PO₄³⁻ obtained)

Calculations-
Substance= 1.0034gm
Weight of empty platinum vessel= 25.4886gm
Weight of platinum vessel containing PO₄³⁻ = 25.7708gm
Net weight of PO₄³⁻ = 0.2822gm
% of Phosphate present in Exhaust = (0.2822 x 100)/1.0034 = 28.1243 %

Lead Pb⁺²-
Substance + H₂SO₄ (sulphuric acid) → heat → filter → C₂H₅OH (Ethyl alcohol) → heat → white ppt. (Pb⁺² confirmed) → filter → substance on wattsman filter paper burn in platinum vessel 700 – 800°C → lead (Pb⁺² obtained).

Calculation-
Substance= 1.0138gm
Weight of empty platinum vessel= 25.4886gm
Weight of platinum vessel containing Pb⁺² = 25.5017gm
Net weight of Pb⁺² = 0.0131gm
% of Phosphate present in Exhaust = (0.0131 x 100)/1.0138 = 1.292 %

Conclusion:
In many tribological applications the variable nature of the performance of any lubricating medium requires different experiments and tests. However the variation in the different constituents of the burnt out residues indicate the performance of the oil while in application. The lead constituents are less than the sulphates and phosphates due to their bad pollution effects. The sulphates and chlorates are found to be lesser than the phosphates by volume. The sulphates and chlorates are the outcome of the formation of acids which may otherwise damage the interior of the engine. The phosphate constituent is found to be more in volume. This component protects the inner surface from corrosion and acidic reactions giving longer life.