CHAPTER I

INTRODUCTION

1.1 Gasoline Composition and Additives Necessary for Internal Combustion Engine(1)-(3)

Motor gasoline consists almost entirely of a complex mixture of hydrocarbons derived from crude oil and boiling between about 30 °C and 220 °C, i.e. containing compounds in the range C_4 to C_{12}. Small amounts of additives are usually incorporated in order to enhance various performance aspects of the fuel.

Motor gasoline is classified according to their octane (or anti-knock) quality: "Regular" grade and "Premium" grade. Gasolines can vary widely in composition even if they are of the same grade. This is because refineries differ in the range of products they supply and so differ in the processes that they have available. Each refinery has to select the processes that will best enable it to meet the quality and volume of all the required products at minimum cost.

The hydrocarbons which make up the bulk of a gasoline are normally categorized into three general types : paraffins, olefins and aromatics. The gasoline component streams are classified by the most important compounds present. A motor gasoline must have an odour that is acceptable to consumers and so must be essentially free of any constituent that has an unpleasant smell.

In the spark ignition engine, gasoline is pumped from the tank and delivered to the carburettor.This is a device, operated by engine section having as its primary function the metering of liquid fuel and air in the required ratio for any given engine operating condition. A secondary function is to atomize the fuel so as to achieve adequate homogeneity of the air/fuel mixture. The amount of mixture is controlled by a butterfly valve or throttle operated by the accelerator pedal. The fuel/air mixture can be enriched for cold starting by various means depending on the carburettor type. The use of fuel injection systems instead of carburettors is becoming more common, in spite of being more expensive, since they do allow a much closer control of the fuel/air mixture. This can give, particularly when used with microprocessors and feed-back controls, improved economy, more power and lower undesirable exhaust emissions.

The fuel/air mixture passes into the inlet manifold where, usually with the aids of some form of heating, vaporization of the fuel is completed. The charge is then delivered to the combustion chambers by way of the inlet valves, compressed by the pistons and fired by the spark plugs. The pressure developed by the combustion process must be smooth and controlled in order to make maximum use of the energy liberated, not only fuel factors but also engine factors play an important part on this. After combustion, the hot gases are exhausted from the cylinders via the valves through the exhaust and silence system, and are finally emitted into the atmosphere. During this whole process, both the physical and the chemical properties of the fuel play important parts.

Gasoline properties

The gasoline sold on the market is a blend of a number of products produced in several processes. By such blending, the properties of the fuel are adjusted to give the desired operating characteristics. Thus, the gasoline, irrespective of its origin, should have the following properties.

(1) Knock characteristics. The present-day measure is the octane rating. The fuel should have an octane rating to fit the engine requirements.

(2) Volatility

a. Starting characteristics. The gasoline will start the engine readily if a portion of the fuel has a low boiling point that will enable a combustible mixture to be formed at the surrounding air temperature.

b. Vapor-lock characteristics. The fuel should have a low vapor pressure at the existing fuel-line temperatures to avoid vaporization in the feed lines and carburettor float bowl, which would prevent or reduce flow of the liquid fuel.

c. Running performance. In general, the fuel with the lowest distillation temperatures is the best.

d. Crankcase dilution. Dilution of the lube oil may occur when the fuel condenses or fails to vaporize in the engine, and a low distillation temperature range is desirable.

(3) Gum or varnish deposits. The fuel should not deposit either gum or varnish in the engine.

(4) Corrosion. The fuel and the products of combustion should be noncorrosive.

(5) Cost. The fuel should be inexpensive.

<u>Gasoline additives</u>

Modern gasoline may be made up of straight-run gasoline (from fractional distillation), cracked gasoline (from catalytic or thermal cracking), reformate (from catalytic reforming), alkylate and polymerized gasolines (produced from gases), with some butane or propane to achieve the desired Reid vapor pressure. Furthermore, additives are invariably required for many purposes.

Antiknock. To reduce or eliminate the knock in engine. Here TEL,TML and scavenger or oxygenated fuels are added.

Deposit modifiers. To alter the chemical character of combustion chamber deposits and so reduce surface ignition and spark plug fouling. (Phosphorus and boron compounds)

Antioxidants. To reduce gum formation and decomposition of TEL (amines, derivatives of ammonia with formula $R.NH_2$)

Detergents. To prevent deposits in carburettor and manifold. (alkyl amine phosphates)

Lubricants. To lubricate valve guides and upper cylinder regions. (light mineral oils)

Metal deactivators. To destroy the catalytic activity of traces of copper (amine derivatives)

Antirust agents. To prevent rust and corrosion arising from water (and air). (fatty-acid amines, sulfonates or alkyl phosphates)

Anti-icing agents. To prevent "gasoline freeze" from water in the fuel, and throttle plate icing from water in the air. (methyl alcohol, isopropyl alcohol)

Dyes. To identify TEL in the fuel.

Knock rating of gasoline

The knock rating of a gasoline is found by comparing the knock with that of a blend of primary reference fuels (PRF). These fuels are n-heptane with an octane number (ON) of 0; and 2,2,4 - trimethylpentane (called isooctane) with an octane number of 100. An octane rating (OR) of 80 indicates that a test fuel will yield the same knock reading in a standard engine under prescribed operating conditions as a solution of 80 parts of isooctane and 20 parts of n-heptane (and the test method must also be specified). The scale is extended above 100 by adding tetraethyllead (TEL) to isooctane.

Single-cylinder variable compression ratio engines, known as CFR engines, are used for knock rating, and were first accepted for this purpose by the Cooperative Fuel Research Council in the USA in 1930.

Briefly the procedure followed is to vary the compression ratio to obtain a standard knock intensity as measured by an electronically controlled knock meter, using an air/fuel ratio the gives maximum knock. When this knock meter reading is bracketed by two reference fuels differing by two octane numbers, the rating of the sample is calculated by interpolation.

Nowadays it is normal to define the antiknock quality of a fuel by three different octane parameters: research octane number (RON), motor octane number (MON), and a number concerned with the octane distribution through the boiling range of the gasoline. The most important of these from a commercial viewpoint is the research octane number (RON), since this is widely used to define octane quality in the market. It is determined by the research or F-1, rating method and relates mainly to relatively mild operating conditions such as are found during cruising and low-speed driving. The motor, or F-2, rating method relates to more severe driving, conditions such as high-speed, high load operation.

Antiknock additives

Although possible, it is not economically feasible to raise the octane rating of gasoline by refining methods alone. Therefore, great quantities of additives are required to obtain the octane ratings demanded by modern, high compression engines. The ideal requirements for an antiknock are :

(1) Low cost per unit increase in octane rating.

(2) No deposits left in the engine.

(3) Relatively low boiling temperature to ensure good distribution in multicylinder engines.

(4) Complete solubility.

(5) Nontoxic

(6) Stable

An additive is called an <u>antiknock</u> if it increases the octane rating and a <u>proknock</u> if it reduces it (sulfur, peroxides, explosives, etc.). The primary commercial antiknock is TEL since it is found to be most effective per unit cost. Iron carbonyl has been tried in Europe but the product of combustion, iron oxide, tended to short the spark plugs and to cause extreme wear of the cylinder and rings. An intensive search is always under way for a completely organic ashless antiknock (such as aniline, ether) but the cost per octane unit increase has always been much greater than for TEL.

The response of a fuel to the additive is called the <u>susceptibility</u> and measured by the change in octane rating per unit of additive. The response of fuel to the addition of TEL, called <u>lead susceptibility</u>, varies greatly from one fuel to another and even for the same fuel when the test conditions are changed. As generalizations for commercial gasolines, the paraffins have the highest response to TEL, with the olefins and aromatics less responsive. The response is proportionately less with increase in amount of additive. It is even further reduced if an antagonist is present. A substance that decreases the response of the antiknock additive is called an antagonist. Conversely,a substance that increases the response to the antiknock additive is called an extender or promotor or synergist.

1.2 Objectives of the Present Study

Due to worldwide lead phaseout in gasoline, many attempts have been made to find other compounds which can replace lead as efficient octane improvers. Such compounds as MMT (methylcyclopentadienyl manganese tricarbonyl) and iron pentacarbonyl were used in Europe and the United States, but they were banned later for the reason that MMT aggraved the emission and air pollution and iron pentacarbonyl reduced the lifetime of valve and other parts of the engine because of its combustion product, iron oxide. In U.S.S.R, thallium compound was used as octane improver but it was also banned because of its toxicity. Another class of compounds, being used at present, is a group of organic compounds, which is of high octane number itself, for example, aromatics, BTX (benzene, toluene, and xylenes) which come directly from refinery process, alcohols and ethers. Alcohols may be blended with gasoline but have many disadvantages : they can cause phase separation with water and can damage rubber lining part in the engine. Ether, MTBE,(methyl tertiarybutyl ether), which is widely used now must be blended in high proportion with gasoline (10-20% by volume) to meet the octane required and it is expensive. Many refiners have tried to improve refinery efficiency such as catalytic cracking and reforming to produce high octane gasoline but this greatly increases the cost of the process. Suitable non-toxic organometallic compounds which could be used in place of lead as octane dope in gasoline would be very useful. A group of compounds selected for detailed investigation in this study were organotin compounds.

These compounds should have many advantages, firstly, tin is in the same group as lead in the periodic table, they should have similar chemical properties. Many previous experiments showed that tin compounds (3)-(6)could act as octane improvers. Such compounds as TET (tetraethyltin) (3), HMDT (hexamethylditin)(4) were used in selected base oil and showed that the antiknock property was improved. Secondly, organotin compounds can solve the pollution problem for its decomposition products, inorganic tin compounds, are non-toxic and very inert. Thirdly, tin metal is an excellent lubricant when allowed to come into contact with moving parts in the engine, thus providing the necessary lubrication and compensated for the loss of lead 's lubricating qualities. Another benefit is tin's properties as an insulator, which will insulate the working surfaces of the engine, protecting it from damage (7).

In the study, the selected organotin compounds were a group of compounds which tend to decompose readily forming tin metal or tin oxide particles in the combustion chamber according to the accepted theory of knock suppression. Therefore, allyl compounds and benzyl compounds were investigated, among these compounds, a novel compound, triallyltin diethyldithiocarbamate, was also synthesized, the common butyl commpounds were also studied and some organotin coordination complexes were synthesized in order to determine the antiknock property.

This study also investigated various methods for the synthesis of organotin compounds, especially direct synthetic methods, in particular for the synthesis of tetraorganotin compounds, and to improve their yields.