B. NATURE, TYPES AND FUNCTIONS OF FUEL ADDITIVES AND THEIR ROLES IN CONSERVATION

by

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1. *LIQUEFIED PETROLEUM GAS (LPG) ADDITIVES*

LPG is a mixture of propane and butane, two hydrocarbons which are gaseous at atmospheric pressure but liquid if higher pressure is applied. They are obtained from natural gas at natural gasoline plants and also from refinery gases. A large volume of the gas can be compressed into a small volume of liquid, simplifying handling problems. Liquefied petroleum gas or "bottled gas" as it is sometimes known is an important domestic fuel in rural and urban communities which have central distributing systems. LPG is widely used as an intermediate material in petrochemicals manufacture. Now, it is also used as motor fuel in trucks and buses.

For safety in handling and in use, LPG must be odorized because the gas mixture is practically odorless. It is required by law to contain a warning agent so that faulty escape of the gas can be detected. For this purpose powerful odorant additives are employed. Ethyl mercaptan, thiophane sulfied, and other petroleum mercaptans and sulfide-type additives accepted for this purpose at a treat rate of 1.5 lb. per 10,000 gals. of LPG. These additive warning agents should not be toxic or chemically active but should normally contribute from 0.2 to 0.4 grain of sulfur per 100 cu.ft. of gas. Such additives should not condense in high-pressure lines at normal operating temperatures and should be insoluble in water. In addition to these properties, it should burn completely in the gas without forming harmful deposits or odorous combinations of products.

2. *GASOLINE ADDITIVES*

The introduction of a new additive in gasoline is a no hit-or-miss proposition. In each instance it is preceded by months and years of research and development work, involving exhaustive testing in the laboratory and in fleets on the road before the additive becomes a commercial reality. Not only must the additive do the job for which it is intended, but it must be trouble-free from the time it enters the fuel tank of the vehicle until the exhaust gases pass out of the tail pipe.

a) *Anti-knock agents*

These are compounds which, when added to a gasoline fuel for spark ignition engines, raise its anti-knock quality, which is expressed in octane numbers. There are three broad classes of compounds from which anti-knock additives are selected: (1) hydrocarbons of natural high octane number, (2) the aromatic amines, and (3) the organometallic compounds.

The hydrocarbon class of anti-knock compounds should be regarded as fuel component rather than considered for their anti-knock effectiveness as additives. The usefulness of the amines appear to be confined to special cases, such as to supplement the tetraethyl lead (TEL) in aviation gasoline. Of the organometallics, there are many which exhibit anti-knock value. The lack of one or more of the other essential qualities in additives, such as solubility, volatility, and low cost, has ruled out all but two, the lead alkyls and iron carbonyl. The latter is lower in cost but increases engine wear because of its abrasive combustion products, thus making its use impractical. Of the lead alkyls, tetraethyl lead and tetramethyl lead, or mixtures of the two are accepted standard anti-knock agents for commercial use in motor gasoline.

Tetraethyl lead/tetramethyl lead, when burned alone in the engine, leaves an "ash" compound largely of lead oxide which has certain deleterious effects on the engine. Organic bromides and chlorides were found to be the most effective scavenging agents to prevent formation of these ash deposits. As used in motor gasoline, TEL is blended with both ethylene dibromide and ethylene dichloride for the effective modification and scavenging of combustion deposits.

TEL itself is a toxic material. Motor gasoline containing not over 3 ml of TEL per gal. is safe as normally handled and this maximum limit is fixed by law.

Commercial benzol or benzene has been blended with gasoline to improve its anti-knock quality. In some instances, 10-30% by volume has been used to make an improved anti-knock but non-leaded gasoline.

A new anti-knock agent, methyl cyclopentadienyl manganese tricarbonyl, is now in an advanced development stage. It is used to supplement TEL in super motor gasolines. In such premium motor fuels, its maximum economic attractiveness may best be achieved as a "promoter" action to TEL. As little as 0.1 gram per gal of this manganese compound gives a higher octane response than greater concentrations of TEL alone.

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b) *Anti-oxidants and Sweetening Inhibitors*

With the commercial production of high-octane motor gasoline through "cracking" processes, antioxidants were introduced into the finished gasoline to counteract excessive gum formation caused by oxidation and polymerization of its unsaturated components. Oxidation, once started, can proceed as a chain reaction and the end product is gum, which may form in storage tanks, refinery lines, and the fuel induction systems of gasoline engines. In addition to clogging fuel lines, carburetor jets, and intake manifolds, gum may deposit on engine moving parts, such as intake valves and piston skirts, causing mechanical failures. Gum formation preferentially removes TEL, with subsequent lowering of octane number. This characteristic is related to the lack of stability of gasoline in storage.

The basic chemistry of gum formation and antioxidant action is quite complicated. Formation of gum in cracked gasoline is delayed or prevented by the small amounts of inhibitors. These usually consist of phenolic or amine-type compounds and they act as negative catalysts.

The main gasoline antioxidants commercially available are:

(1) 2, 6-di-tertiary-butyl-4 methyl phenol or 2, 6–di–tertiary–paracresol (50 lbs. per 1000 bbl maximum).

(2) NN' di-secondary-butyl-para-phenylenediamine (35 lbs per 1000 bbl maximum).

Generally, combinations of phenylene diamine and phenolic type inhibitors are employed to additionally counteract the malodorous effects of traces of mercaptans in the gasoline and the anti-knock effectiveness of TEL.

c) *Metal Deactivators*

Gasoline contamination with trace metals, especially copper impurities from refinery and/or refinery equipment such as copper containing alloys, brass fittings, etc. has been shown to be related to gum formation.

Traces of copper in amounts as little as 10 ppm can exert catalytic effect in gum formation and it is common practice to add a metal deactivator (MDA) to isolate the available copper in the form of a strongly bonded chelate compound. Metal deactivators well known for their activity are N, N'-disalicylidene-1, 2-diaminopropane and N, N' disalicylidene-1, 2-diaminoethane. Usual treat is 1-3 lbs. per 1000 bbls.

d) *Rust and Corrosion Inhibitors*

Rusting and corrosion of ferrous and bimetallic parts in gasoline and circulating systems and storage or in automotive vehicle fuel systems are usually caused by water condensation from the atmosphere, acids from fuel oxidation, or halogen acids from leaded fuel. Such rusting and corrosion can be overcome by incorporating polar or semipolar compounds in the fuel. These additives are oil soluble, of the surface or film-forming types, whose polar molecules absorb on the metallic and on the metal oxide surfaces, thereby preventing water-metal contact. This acts as a barrier against rusting and corrosive material. A few of the well known types of rust and corrosion inhibitors are organic phosphates and sulfonates. One sulfonate type is ethylene diamine dinonyl naphthalene sulfonate. Commercial treat is 10-50 ppm.

e) *Deicing and Antistall Agents*

Formation of ice in fuel lines and carburetors cause engine stalling during cool, wet weather. Vaporizing action of volatile gasoline produces maximum refrigeration of the carburetor throttle plate when the throttle is mostly closed. Carburetor icing begins when the carburetor parts are chilled below 30°F and when the humidity is 65% or higher. To prevent carburetor icing, specially selected and treated alcohols in concentrations as high as 2% are added to gasoline as anti-stall agents. Dimethyl formamide used in concentrations as low as 0.10 volume per cent also provides protection from this type of driving hazard or annoyance.

f) *Pre-ignition Additives*

Under high speed or high-power driving, complex lead halide and lead sulfonate compounds resulting from the combustion of the gasoline form on the spark plug insulators. Because of their low-melting temperatures, the lead halides contribute to the "low shunt resistance" type of fouling by becoming electrically conductive at elevated temperatures and, in effect, short-circuiting ignition. For this type of undesirable effects, phosphorus type of fuel additives are widely used in motor gasolines to modify the effects of undesirable surface ignition and inhibit spark-plug fouling by modifying the deposit on spark-plug insulators. The effectiveness of phosphorus is attributed to the formation of high-melting lead phosphorus deposits which will not glow until 1000°F or higher by chemical alteration with the aid of an accepted pre-ignition additive. A popular compound preignition additive used in leaded gasoline is TCP (tricresylphosphate). Tributyl boron is also used. Recommended concentration is 0.01 to 0.02% by weight.

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g) *Gasoline Dyes*

For color coding and convenient identification of grades of motor and aviation gasolines, fuel soluble organic dyes are used. Most automotive gasolines contain 12-15 lbs. of dye per million gallons whereas aviation gasolines may contain up to 26 lbs. In such minute concentrations, gasoline dyes can never clog carburetor parts or cause noticeable deposits in automotive engines. The red dye of motor gasoline is essentially methyl derivatives of azobenzene-4-azo-2 naphthol and the orange dye is benzene-azo-2 naphthol. The blue dyes are usually derivatives of anthraquinones.

3. DISTILLATE FUEL OIL ADDITIVES

a) *Fuel Stabilizers*

Because of increasing use of catalytically cracked distillates and a growing demand for middle distillate products mainly for domestic or industrial burners and diesel engines, admixtures of these two classes of fuels become inevitable. Straight run fuels added to cracked distillates have poor compatibility characteristics because the dissolved gums in the cracked distillates are precipitated by the straight run fuel. For improved storage and thermal stability, additives are used to prevent gum formation which results to clogging of filters and burner screens. They reduce thermal decomposition which would build up carbon deposits in the burner nozzle and in the combustion chamber. These additives are primarily inhibitors to reduce residue formation or dispersants to reduce particle size, thus improving filter performance and reduce screen clogging. Such additive types include metal petroleum sulfonates, polar polymers, alkyl amines, and various combinations of these. It has been found that metal deactivators of the salicylidene propanediamine type of additives when added to fuels in low concentrations will prevent formation of gels which interfere with filters of oil burning systems. Treatment ranges from 10-150 lbs. per 1,000 bbls.

b) *Cetane Number Improvers*

Formerly diesel fuels in the cetane number range of 50 had to be straight run distillates from paraffin base crudes. With the coming of cracked stock distillates, cetane numbers fell to as low as 37. Even though diesel engine operators discovered ways to operate their engines on lower cetane fuels, problems of maintenance, excessive wear, smoke and deposits were encountered, specially in warm-up and light-load operations. Certain types of additives, such as organic oxides or peroxides in small amounts, improved the ig-

nition qualities of the cracked diesel fuels. Amyl nitrate, as little as 0.1-0.3 per cent volume, is a very satisfactory ignition improver additive for upgrading conventional cracked stable heating oils into diesel fuels of acceptable cetane number.

c) *Anti-Smoke and Order Neutralizing Additive*

With growing concern over air pollution, the exhaust of diesel trucks and buses is often singled out as being particularly offensive. Although diesel exhaust contains much less carbon monoxide and is not as toxic as gasoline exhausts, it is generally more conspicuous. Then, too, diesel exhaust has an objectionable and irritating odor. Thus, even though the diesel engine is a relatively minor contributor to air pollution, it has aroused a great deal of public hostility. The normal diesel exhaust odor is primarily caused by formaldehyde, higher aldehydes, and other partially burnt hydrocarbons.

A specialty additive available in the market for suppressing diesel engine smoke and odor obnoxiousness is a special barium formulation, used with a recommended treat of 0.31% volume. This material is marketed by Esso Chemicals under the material trade name of "Paradyne 11."

4. RESIDUAL FUEL OIL ADDITIVES

a) *Sludge-Dispersing Agents*

Many residual fuels are high in sludge-forming unsaturates. Also, sulfur, ash, and sometimes moisture content, specially salt water, are undesirably high. Sludging in storage and corrosion and slagging in boilers and gas turbines are problems frequently met when such fuels are used. In service, sludge frequently forms in refiners' tanks, and, more frequently, in the tanks of distributors and customers who receive their supplies from different sources. This lack of compatibility of a given fuel in blend with a second fuel complicates the situation. In addition to occupying valuable storage space in the tanks, this sludge may plug suction lines, strainers, and fuel nozzles; interfere with heat transfer in heaters, adversely affect combustion.

Sometimes called "dissolving" compounds, sludge-dispersing agents are generally coal-tar-derived products such as methyl and dimethyl naphthalenes. Use of these materials varies from 50-150 lbs. per 1,000 bbls.

b) *High-Temperature Anti-Corrosion Agents*

Vanadium and sodium constituents in residuals are related to high temperature corrosion at combustion zones, such as in boiler super-heated regions, gas turbine rotor blades and nozzle partitions, and on diesel-engine pistons, cylinder liners, valves, and parts. The higher the vanadium content of the ash, the more rapid the oxidation and corrosion rate at temperature above 1,200°F (the melting point of the vanadium constituents). In addition, as the ratio of sodium to vanadium pentoxide increases, the rate of attack increases.

Generally, sodium is in the fuel oil as natural constituent, but it may be introduced during the refining process or by salt-water contamination. Salt-water contamination not only raises the a-V ratio but also makes it more difficult to burn residuals in boilers, gas turbines, and diesel engines.

High temperature corrosion can largely be eliminated in fuel oil fired equipment by use of magnesium bearing additives in the fuel. Magnesium can be added in the form of oil soluble compounds such as the naphthenate, as an aqueous solution of magnesium sulfate, or as a suspended finely divided solid, such as an oxide, carbonate, sulfate, or dolomite. Obviously, if an aqueous solution or a finely divided solid is used, it must be added by the user at the time of firing. The aqueous solution can be injected into the oil feed line or into the firebox by means of suitable proportioneering equipment. Similarly, the finely divided solids can be slurried with a portion of the fuel oil and added in the proper ratio to the fuel oil feed line. Additive treat could vary from 125-6,000 lbs. per 1,000 bbls., depending on the nature of additive used and equipment under consideration.

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