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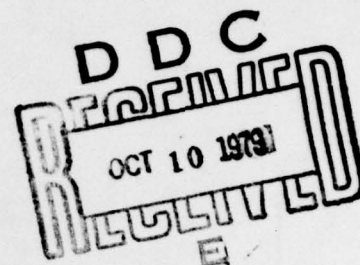
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SOOT CONTROL BY FUEL ADDITIVES
-- A REVIEW

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20 Abstract (continued)

through additive use are discussed. Iron additives and their combustion products are relatively non-toxic, whereas the popular manganese additives and their oxides are fairly hazardous. Generally, only water soluble barium compounds are toxic, and these typically constitute only 25 percent of the barium compounds in diesel engine exhaust. Additives are only recommended for short-term use, combustor design modifications being the economically preferred long-term solution.

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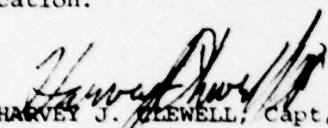
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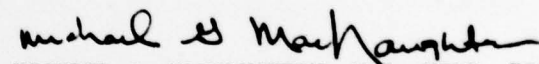
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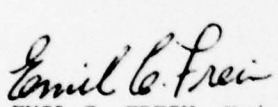
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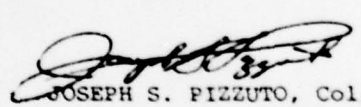
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SECTION 1

INTRODUCTION

Soot is the particulate matter resulting from incomplete combustion of hydrocarbon fuels. When present in sufficient particle size and quantity, soot in exhaust gases constitutes a black smoke. Soot formation is generally undesirable since it causes environmental pollution, combustor design limitations, and tactical problems in military applications.

Although soot is not the most abundant pollutant, it may be one of the most hazardous since soot particles are of the proper size (50 to 2000 Å) to be inhaled deep into the lungs (1). The observation that soot can cause cancer of the skin in man was first made by Pott in 1775 (2). The polynuclear aromatic hydrocarbons (PAH) adsorbed on soot are believed to be responsible for this effect (3,4), as many PAH are known to be carcinogenic (5).

Turbine combustors are usually limited by the temperatures which their walls can withstand (6). Increased emissivity and higher radiative heat transfer caused by soot formation in the combustor can cause overheating and damage. Excessive quantities of soot particles can erode turbine blades and cause carbonaceous deposits leading to fuel spray distortion. These problems would become even more serious with any trend toward more aromatic fuels (7). Militarily, a fuel-rich primary combustion zone is desirable as it improves high altitude relight capability (8). However, a sooty exhaust trailing jet aircraft is equally undesirable since it enhances detection by an adversary (8). The U.S. Navy has also reported problems with carbon deposits left on aircraft carrier decks (8), and in 1965 launched a program aimed at ridding their planes of smoke (8,9).

Soot formation in aircraft turbines first received attention by the Air Force during the Korean conflict. However, inquiries to pilots produced no complaints, and the problem was temporarily set aside (11). The first commercial jet aircraft introduced in 1959 were marginal on power, and therefore used water injection during takeoff. This generated much more soot than dry operation, probably by prematurely quenching combustions reactions (11). Complaints about jet smoke from residents in areas around the Los Angeles International Airport provoked a study (12) which showed that although the overall contribution to air pollution by aircraft in metropolitan areas was only 1 or 2 percent of the total, it was responsible for around 10 percent of the total in the immediate area of the airport (12,13). Nevertheless, industry was slow to respond, probably since even a very smoky exhaust resulted in only a minor loss (less than 1/2%) in combustion efficiency (8,10), and because the health hazards of soot and PAH were not as well documented as they are today (3,5).

Finally, in 1968 Pratt and Whitney released information on a new combustion chamber for the JT8D engine which had been successful in reducing smoke emissions (13). However, problems with soot formation still exist, especially with the new and more powerful turbines employing higher combustor pressures and heat release rates (11).

Most investigations of jet engine emissions have reached the conclusion that combustor design modifications are the best method of assuring clean exhaust (6,8,14-16). Design modifications are undoubtedly the most economical long-term approach, but they may not be possible in all cases. Considerations such as power and reliable performance at all operating altitudes sometimes make other solutions more desirable. The use of fuel additives is one such solution which has gained much attention.

Additionally, the chemical properties of fuels are known to have a substantial effect on sooting tendency. In well-mixed systems burning with excess oxygen, acetylene has shown the least tendency to form soot, followed by (in order of increasing tendency to form soot) alkenes, alkanes, benzenes, and naphthalenes (7). Thus, as petroleum based fuels dwindle in supply and are supplemented by the more aromatic coal-derived liquids, more problems with soot formation can be expected. The staged combustion systems now being considered for NO_x reduction also increase the tendency for sooting problems due the lower-temperature, fuel-rich primary zone. Thus, even the best possible design modifications may still need help from fuel additives to keep soot formation within acceptable levels.

SECTION 2

ADDITIVES IN PRACTICAL COMBUSTION SYSTEMS

2.1 BACKGROUND

The first use of flame additives to reduce soot formation was reported by Bartholomé and Sachsse (17) in 1949, based on tests performed in fuel-rich hydrocarbon flames in the German synthesis gas industry. Salt solutions of "almost all elements in the Periodic System" were injected as fine mists into a region of the flame in which the primary decomposition of the fuel was thought to have already occurred. Soot reductions as high as about 75% (unspecified basis) were reported with the transition metal nickel, although the alkali metals and alkaline earths were also effective. Additionally, the soot collected was observed to be "more finely grained" when the additive was employed.

2.2 UTILITY AND DOMESTIC BOILERS

Additives were tested in an oil heating combustor by Weeks, Clinkenbeard, and Soltis in 1959 (18). At a specific weight concentration of metal, Ferrocene (dicyclopentadienyl iron) was most effective, followed in order by Ni, Co, Mn, Pb, Mg - all in the form of naphthenates. Lead naphthenate was found to be more effective than tetraethyl lead, but apparently this was the only organic-substituent effect observed. However, even with the most effective additive tested, the concentrations necessary for a significant effect were considered too costly for long term use. Additionally, the measurement technique used was based on the allowable reduction in excess air at the no-smoke point, a technique which unfortunately cannot distinguish between a reduction in the weight of soot emitted and a shift in particle size distribution which makes the same amount of soot less visible.

Vaerman (19) reported in 1964 the testing of various metal naphthenates in a commercial central heating plant using a pressure jet gun-type oil burner. Results were correlated based on a reduction in Bacharach smoke number, i.e., the shade of a white filter paper through which a standard volume of the flue gas has passed. A reasonably good correlation between Bacharach smoke number and weight of soot in the flue gas was obtained. At a metal weight concentration of 100 ppm, and with 40% excess air, the most efficient metal was copper, followed in order by cobalt, manganese, iron, nickel, lead, potassium, and barium. The Bacharach smoke number decreased from about 7 to 3 with copper, corresponding to about an 80% by weight reduction in flue gas soot. Additional tests with different solubilizing organic groups showed that only the nature and concentration of the metal were important in soot reduction. Vaerman also discussed corrosion-reducing additives in detail.

Riggs, Wilkinson, and Wolfe (20) studied the effectiveness of several additives at a concentration of 0.1 grams of metal per gallon of No. 2 fuel oil when burned in a domestic heater unit. A commercial fuel additive, methylcyclopentadienyl manganese tricarbonyl (MMT), achieved an 80 percent reduction in particulates, followed by cobalt naphthenate (70 percent), manganese naphthenate (65 percent), chromium carbonyl (60 percent), calcium sulfonate (45 percent), nickel carbonyl (40 percent), and lead naphthenate (30 percent). Unfortunately, a summary (21) of this paper (20) did not state the base level of particulates (without any additives), the excess air used in firing, or the method (gravimetric or optical) used to determine the particulate reductions. When viewing the wide range of results reported for the same additive in even similar combustion systems (and conditions), these correlating parameters (or ones of a similar nature) would appear to be crucial if the observed results are to be of any use in predicting the performance of the additives with similar combustion systems and conditions.

Finfer (22) conducted a brief literature survey on combustion improvement additives for fuel oil combustion in boiler systems. The results of Hartle and McGuire (23) with an iron chelate in rather large concentrations of 0.01 - 0.08% by weight of fuel were shown to be more effective than hydrazine (24) at 0.05% by weight, or copper sulfonate (19) at 0.01% by weight. Finfer also pointed out that many of these experimental results were based on smoke numbers and other optical techniques, and indicated that gravimetric tests would be more reliable for measuring soot reductions. He was also apparently the first to warn that some of the metal oxides formed by these additives and emitted in the stack gases might be toxic.

Kukin (25) reported on the use of additives in oil-fired furnaces to improve boiler cleanliness, cut corrosion, and reduce stack emissions. Magnesium oxide was shown to be effective in the first two categories, while manganese was shown to reduce particulate emissions by as much as 80% by weight. Tests were carried out in a package boiler burning heavy asphaltic bottoms and producing 200,000 lbs of steam/hr at 900°F superheat with 900 psi pressure. Using manganese in a concentration of 45 ppm metal by weight, flue gas particulate matter decreased from 0.17 to 0.04 mg/scf, with a reduction in carbon content of the emitted particulate matter from 72 to 31% by weight.

One of the most extensive testing programs on the effects of fuel additives on pollutant emissions from distillate-oil fired furnaces was conducted by Martin, Pershing, and Berkau (26) of the U.S. Environmental Protection Agency. Released in 1971, their report showed the results of tests with some 206 commercial additives. Additives were all tested with 20% excess air and a uniform No. 2 distillate oil of 25% aromatic content and a mass ratio of carbon to hydrogen of 6.62 to 1 (empirical formula $CH_{1.81}$). Additive concentrations were based on those recommended by the manufacture as well as a constant 0.5 millipore metal per kilogram of fuel (if different). Two sandwich transition metal complexes, di-cyclopentadienyl iron (Ferrocene-20% Fe) and methylcyclopentadienyl manganese tricarbonyl (MMT-25% Mn) were found to have the greatest effect on particulate emissions from a cost/effectiveness viewpoint. A chemical analysis of the 206 additives revealed that more than half had a total metal content greater than 0.1 percent. However, of the 14 different metals represented, only the additives containing at least one of the transition metals, iron, manganese, or cobalt, significantly reduced particulate emissions under the conditions tested. The seven most effective additives, and the ratio of particulates with the additive

to particulates without the additive, are listed in Table 1. The authors also warned of the possibly toxic emissions caused by the use of some of these additives, and pointed out that additional tests which they conducted led to the conclusion that commercially available flame retention devices could reduce particulate emissions more than any of the additives tested.

The seven most effective additives referred to above have also been tested by the same authors in a residual-oil fired boiler (27).

TABLE 1. DISTILLATE FUEL-OIL ADDITIVES THAT SUBSTANTIALLY REDUCE TOTAL PARTICULATE EMISSIONS [from Martin, Pershing, and Berkau (26)]

Additive	Concentration		Composition	Total particulate ratio
	Weight	Molar ^a		
Arapahoe Ferrocene	1:7150	0.50	20% Fe	0.53
Ethyl CI-2	1:9000	0.36	18.0% Mn	0.56
Commercial Chemical Improsoot	1:150	0.50	0.3% Ca ^b 0.1% Ca ^b	0.57
Gamlen DP 231	1:110	0.50	0.2% Mn 0.1% Fe	0.61
Fuel Combustion Corp. Fuelco SO ₃	1:500	0.10	0.25% Mn	0.64
Commercial Chemical Formula LSD	1:200	0.40	0.9% Co	0.68
Industrial Chemicals Watcon 130	1:500	0.05	0.15% Fe	0.69

^a Millimoles per kilogram

^b One of these two entries is probably cobalt

An extensive review of combustion additives for pollution control has recently been compiled by Krause, Hillenbrand, Weller, and Lockin (21). This basic review covers virtually all types of combustion systems-boilers, gas turbines, internal combustion engines, and some laboratory studies, as well as several different fuels including distillate oils, and even coal. All pollutants are categorized, including: soot and particulates, polycyclic organic matter (POM), flyash, NO_x, and SO_x. The general conclusions are that fuel additives can be very effective for flyash and carbon particulate removal, less effective for POM removal, only very weakly effective against NO_x, and have virtually no effect on total sulfur emissions, although SO₃ can be reduced.

The review of Krause et al. was conducted as a preliminary step to an experimental evaluation of fuel oil additives in boilers by Giammar, Weller, Lockin, and Krause (28). Their program was executed in a 500 kw commercial fire-tube package-boiler under conditions of variable load, cyclic operation, short term (2 hour), and long term (60-80 hour). Twenty-four fuel additives were evaluated while firing residual oils, and eleven while firing distillate oils. The majority of the experiments were conducted under 80 percent load. The distillate oil was burned with 8 percent excess air (14 percent CO_2) and the average particulate content of the exhaust was about 14 mg/Nm^3 (carbon content of less than 1 percent). Predictably, under these relatively clean conditions, none of the additives achieved a particulate reduction, and more than half actually increased the amount of particulate collected due to added metallic compounds. The two different residual oils had (without additives) baseline particulate concentrations of 72 and 89 mg/Nm^3 . A mixture of iron and barium naphthenates (27 ppm Fe, 51 ppm Ba) achieved the greatest particulate reduction (49 percent) with the remaining particulate being all ash and metals (no carbon). Generally the most effective additives contained transition metals (Co, Mn, Fe) and alkaline earths (Ba, Ca) in concentrations of 20 to 50 ppm metal by weight. It was determined that the mass of particulates in the respirable range was reduced by the additives tested.

2.3. GAS TURBINES

Despite almost a decade of use in boilers and furnaces, additives for smoke reduction were apparently not tested in gas turbines until 1967. Toone (10) conducted experiments with Ferrocene and Lubrizol 565 (a commercial additive containing an organic derivative of barium) in a Rolls Royce Dart engine. A 0.05% concentration of ferrocene (by weight) did not give any evidence of carbon reduction, but Lubrizol (0.25% Lubrizol by weight) did give a significant reduction. Toone observed that these results were exactly opposite to that expected based on smoke numbers that he obtained with a lamp burning Avtur fuel (an aviation kerosine) and the additives. In the lamp, ferrocene indicated an ability to reduce smoke, while Lubrizol 565 indicated a greater tendency to smoke. The Lubrizol additive also had the unsatisfactory feature of leaving barium oxide deposits on the turbine and the inside of the jet pipe.

Shayeson (11) evaluated ten commercial fuel additives available in 1967 in a test rig consisting of a General Electric J79-8/15 combustor with a P5 fuel nozzle and a JP-5 fuel. Test rig results were based on visual estimate of smoke density, the attenuation of visible light using a photocell and recorder, carbon collected by gas sampling through a porous ceramic crucible, and several other methods. At the same metal concentration (0.02% metal by weight) ferrocene and another iron compound (unidentified) were about as effective as a barium compound (also unidentified) and slightly more effective than a manganese compound (later identified by Fiorello (8) to be MMT). However, other considerations including availability, cost, and physical properties favored the manganese compound (MMT) despite the small performance disadvantage. Additives containing alkyl nitrates, boron, lead alkyls, and organic peroxides were found to be ineffective. Further tests of ferrocene and the manganese and barium compounds were conducted on the ground in a J79-8 engine. The barium additive (0.1% volume) eliminated almost all smoke at

military (high) power, but after 2 1/2 hours the engine stalled due to thick white deposits of BaCO_3 in the combustor and turbines. Ferrocene (0.1% vol.) reduced smoke by 90%, and appeared to have no adverse effects after 5 hours, but did leave all interior engine surfaces coated with thin deposits of dusty brown iron oxide. The manganese additive was effective at lower concentrations (0.04% vol.), and also showed no operational difficulties after 5 hours, despite thin dusty deposits of black cubic Mn_2O_3 and orange tetragonal Mn_3O_4 .

After more safety checks, flights tests were conducted with the manganese additive, although at slightly higher concentrations (0.08% additive by volume). The results showed more smoke than the ground tests, this being attributed to the lower power levels used in flight. [In the ground tests all three additives had shown more effectiveness at the higher power levels than at normal (cruise) power.] It was also concluded that the solid exhaust products formed with the manganese additive caused no major adverse effects on J79 engine operation after 100 hours. This conclusion was more optimistic than the results obtained by Pichtelberger et al. (29) in 1966. Based on tests of this same manganese additive (which contains MMT) Pichtelberger reported that some engines showed performance losses with time of operation due to the accumulation of manganese oxides on critical areas of the turbine.

Shirmer (16) has summarized work conducted at Phillips Petroleum Company by both himself and Bagnetto (9) using a small-scale two-inch combustor design to yield results similar to gas-turbine engines. Several different aviation-turbine kerosenes of different hydrogen content were evaluated, as were three different organometallic additives containing manganese, barium, and calcium. Based on optical density measurements in the exhaust, three different additive concentrations, (0.012, 0.024, and 0.036 gram-atoms of metal per gallon of JP-5 fuel) and various combustor inlet conditions, it was concluded that the additives are most beneficial at intermediate turbine-inlet conditions (10-15 atm; 1500-1700°F), and that additive type and concentration were both important. Unfortunately, the most effective additive and the optimum concentration were not specified. Electron micrographs of soot collected with and without the barium additive revealed no significant differences in the soot size or morphology, although the difficulty and subjectivity of particle characterization from this type of simulated gas turbine combustor was pointed out.

Friswell (15) also evaluated several additives in a small-scale combustion rig designed to simulate gas turbine combustion conditions. Barium, manganese, and iron in the form of Lubrizol 565, Ethyl CI-2 (MMT), and ferrocene, respectively, were added to an aviation kerosene fuel (Avtur) and burned under a variety of conditions. Soot was analyzed by both calibrated smokemeter and by filtration/weighing. Preliminary experiments established that manganese and iron had almost identical effects on exhaust carbon over a wide variety of the test conditions, and therefore further examination was limited to only barium and manganese. The effectiveness of the manganese additive was found to be very dependent on the air/fuel ratio (AFR, 15 = stoichiometric) and to increase as the exhaust gas temperature increases. Barium effectiveness was relatively independent of the AFR, and 250 ppm was able to remove carbon completely at an AFR of 80/1. Manganese at a 100 ppm concentration and 35/1 AFR removed 73 percent of the carbon.

Pagni and Hughes have done extensive testing of methylcyclopentadienyl manganese tricarbonyl (MMT, Ethyl Corporation CI-2) including a 1972 report with Giovanni and Sawyer (30) and a 1973 report with Novakov (31). All experiments were conducted using a fairly clean-burning, model gas turbine combustor and JP-4 jet fuel (H/C = 2/1). The baseline emissions (no additive) collected with a quenched sampling probe ranged from 0.15 to 0.45 gm/kgm of fuel. Typical turbojet and turbofan engines were reported by Giovanni and Sawyer (30) to have emissions in the range 2.0 to 14 gm/kgm of fuel. The use of MMT (0.06% by volume) increased the emissions index at the chamber exit by about 0.5 gm/kgm of fuel. By assuming the carbon mass emission was the same with and without the additive, Giovanni and Sawyer were able to use a mass balance on manganese to attribute the increase in particulate mass to solid phase manganese oxides. Without the additive, the smallest of the soot particles were typically 0.1 μ m in diameter and thus efficiently scattered visible radiation. With the additive, the exhaust particles of manganese oxides and carbon were typically 0.05 μ m in diameter, and showed a significant reduction in agglomeration.

Further work by Novakov et al. (31) led to a power law $n(r) = cr^{-b}$ (b, c constants) to describe the measured size distribution of the particles emitted by the model gas turbine combustor. They concluded that the manganese additive redistributed the mass to smaller size particles where it was no longer visible. Neutron activation analysis determined that virtually all of the manganese added to the fuel was being emitted, and x-ray photoelectron spectroscopy determined that the emitted manganese was in the 2+ oxidation state as MnO. The authors in both papers (30,31) warned of the toxic effects of the manganese emissions, and urged that other methods of particulate emission suppression be employed.

Ethyl Corporation (32) has conducted a study of their own additive, MMT, in three different gas turbines (15, 20, and 30 megawatts) using a No. 2 fuel oil. Stainless steel sampling probes were used to collect exhaust sample spots which were then tested by a photovolt reflectometer and reported in either Von Brand or Bacharach units. Particulates were also collected on glass fiber filters to determine total particulates as well as carbon and manganese content. Using concentrations of 20 - 100 ppm by weight of manganese, MMT was claimed to reduce smoke and carbon particulates by 50 - 90%. The greatest reductions in emissions were observed at higher Mn concentration and higher load conditions. The smoke data were observed to fit a semilogarithmic relation, $\log_e S = A - kx$, where A and k are empirical constants, x is the additive concentration in ppm Mn, and S is the Bacharach smoke level (or 100 - Von Brand smoke reading). By using a different set of empirical constants for each of the three turbines, as well as each of the various load conditions tested at each turbine, a reasonably good correlation was obtained.

Champagne (33) analyzed the data obtained by Ethyl Corporation (32) and fitted the results to theoretical expression based on two independent oxidation phenomena, one thermal and one catalytic. The general form is:

$$\Delta C = \frac{k_1 [\text{Mn}]}{k_2 [\text{Mn}] + k_3}$$

where ΔC is the carbon reduction due to the Mn additive, $[Mn]$ is the concentration of Mn in the fuel as MMT, and $k_1 - k_3$ are constants, assuming the secondary zone temperature distribution is uniform and the unit is operating at a steady load. This theoretical expression does not appear to fit the data as well as Ethyl Corporation's empirical relationship, even though it contains an additional constant. Similar to Ethyl's expression, it appears to require new constants for each of the load conditions tested at each of the three turbines.

Champagne and his co-workers at General Electric also tried to verify Ethyl's conclusions with on General Electric MS 7000 gas turbine run at essentially constant load with No. 2 distillate fuel. Particulate emissions were measured by the technique defined in the Los Angeles County Air Pollution Control District Source Testing Manual (34) as well as the U.S. EPA method (35). Both of these methods are gravimetric, differing only in the extent to which particulates are collected from the sampling probe, filters, and connecting glassware. Hilt and Giovanni (36) have described the application of these and other techniques to gas turbines.

Carbon emissions were essentially eliminated with 31 ppm Mn in the fuel. However, the initial percentage of carbon in the particulate was so small (3% by weight) that the total particulate emissions with the additive actually increased. This was attributed to manganese oxides in the exhaust. The amount of the particulate increase was different for each of the two collection methods, with the LA method appearing to collect much more than the EPA method. In reality, this difference was largely shown to be caused by severe hydration of the particles in a wet impinger train required in the LA method. Nevertheless, the addition of MMT to an essentially already carbon-free gas turbine definitely resulted in an increase in the emitted particulates.

Hersh, Hurley, and Carr (37) conducted experiments with iron, manganese, and a manganese/barium mixture as additives to a number two fuel oil fired in a 20 megawatt utility gas turbine. The main objective of this investigation was not to evaluate the effectiveness of the various additives, but to characterize the exhaust particulates according to composition, size, and metal content. Samples were collected according to U.S. EPA Method 5 with heated quartz sampling probes. Metal identity and concentration in the exhaust was determined by neutron activation analysis (NAA) and atomic absorption spectroscopy (AAS). Particle sizing was achieved with a Thermosystems Model 3100 electrostatic aerosol analyzer (EAS) and a scanning electron microscope (SEM) coupled with energy dispersive x-ray analysis.

The results showed a small increase in the total mass appearing as larger particulates. This increase was attributed to particles containing the additive base element, which had a mean diameter of 1.3 microns. The additive base element was not found in any particles below 0.5 microns. Sixty to seventy percent of the Mn (by weight) from the additive containing only Mn was recovered in the exhaust, as MnO (90%) and Mn_2O_3 (10%). The Mn/Ba additive yielded only 30% metal recovery in the exhaust, with about two-thirds as MnO and one-third as Mn_2O_3 . Forty to fifty weight percent of iron from the third additive was recovered, 15% as FeO and 85% as Fe_2O_3 . Theoretical

derivations based on Mie scattering theory by Ensor and Pilat (38) and others (39,40) have led the authors to conclude that the major decrease in plume opacity was due to a reduction in mass loading resulting from the additive use, with only a small contribution due to the slight increase in particle size.

Blazowski (41) recently (1973) reported on the current U.S. Air Force program to use fuel additives to reduce emissions from aircraft gas turbines. The report also includes summaries of two experimental programs conducted by Champagne (42) and Shaw (43). Problems encountered in employing the additives (decrease in fuel thermal stability, hot section deposition, and afterburner spraybar plugging) are discussed along with possible solutions to each problem. Blending several additives to achieve the best results from each is one of the major solutions proposed for investigation. Universal use of fuel additives did not appear cost effective, but use in an on-demand basis or in specialized applications (such as in engine test cells) was found to be justified. Blazowski's review led to the conclusion that iron and manganese compounds generally appeared to be the best candidates for smoke abatement fuel additives. Redesign of existing engines (retrofit) for smoke abatement, although expensive, was considered to be the best long-term solution.

The U.S. Navy (44) and Air Force (45) are currently in various stages of programs aimed at finding safe and effective fuel additives to reduce or eliminate pollutants from their aircraft. The motivation for these extensive programs is easily understood in view of the statement by Richter (46) that retrofitting the entire USAF turbine engine inventory (at \$30,000 per engine, 1973 estimate) would cost approximately one billion dollars. The ultimate goal of these programs is to find safe additives for use in-flight, but currently the emphasis is to find additives for engine test cell use.

Ethyl Corporation's Combustion Improver Number 2 (MMT) was the most cost effective additive studied (47). However, the Navy rejected test cell use of this additive (47) due to the suspected toxicity of its combustion products, as well as the known toxicity of the additive itself (31, 48, 49). Ferrocene has also been shown to be very effective (44), although some engine designs have had problems with deposits of iron oxide. The many engine types are currently being evaluated on an engine-by-engine basis for possible ferrocene use. Navy (47) and Air Force (50) studies have indicated ferrocene is reasonably safe for additive use.

2.4. DIESEL ENGINES

Smoke suppressant additives have also been extensively tested and shown to effectively reduce or eliminate black smoke from diesel engines. Surprisingly, barium appears to be the metal of choice for this type of application, rather than the manganese or iron so often used in boilers and gas turbines.

Ray and Long (51) experimented with several non-metallic additives for diesel engine soot and PAH suppression. The authors concluded that t-butylhydroperoxide was a more effective additive than 1-nitropropane, ethyl nitrate, or nitroethane. Salooja (52) had previously reported all of these additives were powerful promoters of the combustion process. Five percent by volume

t-butylhydroperoxide reduced total particulates by about 30% and benzo[a]pyrene by more than 50% (51).

Norman (53) reported on the effectiveness of a 5% by volume addition to diesel engines of a commercial (Lubrizol) smoke suppressant additive containing barium. Measurements made with an optical technique (Hartridge Smokemeter) on 4, 6, 8, and 12 cylinder engines typically showed from 30 to 50% reduction in opacity with the additive. Laboratory tests, as well as a commercial diesel engine which had operated for 35,000 miles on treated fuel, showed an additional bonus. Fuel injector nozzles, exhaust valves, and most other engine parts were much cleaner and showed less wear than normal. Small ash deposits which did accumulate in some combustion zones were easily crumbled and expected to cause no adverse affects on operation.

Golothan (54) has written one of the most extensive and often cited reports on the use of barium-containing fuel additives in diesel engines. Effectiveness in smoke reduction was determined gravimetrically and with a Hartridge smokemeter. The two techniques correlated very well, showing that the optical density of the exhaust for a 1 cylinder, direct injection, 1.4 liter unit, was reduced 40 - 50% with 0.05% by weight of barium in the fuel. Tests in a 6 cylinder diesel truck driven for approximately 35,000 miles with U.K. DERV fuel and 0.075% wt barium additive showed an average reduction of 20% in exhaust smoke opacity. The largest reduction in all tests was obtained at the higher load conditions. Loose and flaky engine deposits were observed, although the effect on engine performance was minimal. It was assumed that the deposits tended to form and break away continually until an equilibrium level was reached. Nevertheless, the smoke level was observed to vary (and occasionally get quite high) due to these deposits, and thus additive modifications were attempted. The incorporation of dispersant properties (unfortunately not described) in the additive reduced chamber deposits and resulted in a low smoke level throughout.

Golothan also conducted tests for possible PAH reduction by the additive. These were unfortunately inconclusive, although a slight PAH reduction may occur in 4 or 6 cylinder engines.

Miller (55) has evaluated a Lubrizol Corporation diesel smoke suppressant additive (SSA) in 21 European and 5 American diesel engines. The results with this barium-containing additive were measured by Hartridge, Bosch, or Von Brand smoke meters. A smoke reduction curve based on these results was observed to correlate well with the actual weight of soot collected. While the results varied from engine to engine, typical exhaust opacity was reduced by about 35% (from about 55 to 20 Hartridge units) with 0.5% volume of SSA. Combustion chamber deposits were negligible, and valves and injectors were generally in good or excellent condition. Ring and injector wear was also reduced by the additive. Laboratory studies typically showed a 1% increase in fuel economy with the additive, and fleet tests as high as 4% improvement. Miller also cited a report by Deeter (56,57) which showed similar smoke reduction and reduced valve and injector wear.

McConnell et al. (58) has summarized the previously discussed work of Golothan (54) and Miller (55), as well as other work on diesel engine exhaust

smoke and barium fuel additives by Howells (59) and Vulliamy and Spiers (60). The generally good results, previously discussed, are further supported, but little significant new work is presented. The authors conclude that barium-based anti-smoke additives should have a strong future in diesel engine application.

The results of most of the major practical studies of soot reducing additives are contained in this report. In addition to additives designed for soot reduction, Salooja (61) has reviewed many additives for abatement of high and low temperature corrosion problems, and Agius et al. (62) has included a discussion of flow improvers.

2.5. MMT

Methylcyclopentadienyl manganese tricarbonyl (MMT) is a commercial fuel additive (24.7% Mn) available from Ethyl Corporation as Combustion Improver Number two (CI-2). It is a liquid additive suitable for blending with petroleum fuels and has a well-established ability to reduce carbon emissions in boilers (22,26) and gas turbines (32,47). Consequently, it appears to be the most popular smoke suppressing additive on the commercial market (30).

The additive is most effective in very smoky exhaust gases which have a large percentage of unburned carbon. Tests of MMT in relatively clean "smokeless" combustors (whose exhaust is largely ash) have shown that particulate emissions are often increased (28, 30, 33) probably by adding manganese oxides to the exhaust.

For virtually all of the combustion systems tested there existed an optimum concentration of MMT for maximum smoke reduction. Exceeding this optimum concentration not only does not provide further reduction in particulates, but in most systems resulted in an increase above the minimum particulate level already achieved (15,31).

MMT has been tested as an octane booster to replace tetraethyl lead in gasoline engines. However, General Motors, Ford, and Chrysler report that the additive increases hydrocarbon emissions in gasoline engines, and contributes to plugging in catalytic converters (63). Ethyl Corporation has disagreed, reporting no "significant" effects on exhaust emissions, but a definite octane rating boost (63). The EPA has recently agreed with auto manufactures and banned the use of MMT in gasoline.

Cyclopentadienyl manganese tricarbonyl is known to be toxic at low concentrations (26,48), but apparently the methyl derivative has not been as extensively tested. The combustion products of MMT are dependent upon temperature, but typically include MnO , MnO_2 , Mn_2O_3 , and Mn_3O_4 . The toxicity of these compounds in the quantities in which they are emitted is currently a topic of controversy (26,30,31).

The mechanism by which MMT is believed to act to reduce carbon emissions is discussed in a later section.

2.6. HEALTH EFFECTS

Many authors (26,30,31,37,47,48) have questioned the use of fuel additives to reduce smoke emissions on the grounds that the metal oxides emitted by the combustion of the additives may be more toxic than the soot they eliminate. The three most common metals appearing in additives are manganese, iron, and barium. The toxicity of the combustion products of each of these metals is discussed below.

Manganese usually appears as either MnO (31,37), MnO_2 (26), Mn_2O_3 or Mn_3O_4 (37) in the combustion products of boilers (26) and gas turbines (30, 31, 37) using a manganese additive. The relative amounts of these oxides is dependent upon the temperature of operation. A high atmospheric concentration of these oxides may result in (a) chronic manganic poisoning, a disease of the central nervous system, (b) manganic pneumonia, or (c) catalytic oxidation of other air pollutants to more undesirable compounds (48). These diseases have been reported in manganese miners exposed to the corresponding dust, and factory workers in plants that produce various manganese alloys (48). Both diseases are fatal if the exposure is long enough (48).

Iron additives and the oxide combustion products are probably the safest of the three metals discussed herein. Animal feeding studies with ferrocene (the most popular iron additive) show almost complete absence of toxicity (64). Exposure to iron oxides in high concentrations is irritating, and occasionally causes siderosis, a benign lung condition. Deaths due to iron oxides are rare, usually only appearing in iron ore miners exposed to mine dust for long periods of time.

Barium compounds are usually only toxic if water soluble (65). The most common barium compound, barium sulfate, is insoluble and generally nontoxic. Barium compounds omitted by diesel engines using a barium fuel additive have been extensively investigated by Golothan (54). He concluded that typically less than 25 percent of the barium emitted by diesel engines was in the form of soluble barium compounds, (usually barium carbonate). The majority of these soluble barium compounds exist as solids, and little work has been done to determine their atmospheric concentrations or toxic effects (65). However they are almost all poisonous if ingested (65).

SECTION 3

BRIEF REVIEW OF CARBON FORMATION AND BURNOUT

In order to better understand the influence of additives on the soot formation process, it would be beneficial to first understand the process of soot formation and burnout in the absence of additives. However, soot formation in hydrocarbon flames has been studied for over a century and no clear picture of the process has yet emerged (7). Detailed discussions of the many mechanisms proposed to explain the chemistry and physics of the soot formation process are available in reviews by Street and Thomas (66), Palmer and Cullis (67), Gaydon and Wolfhard (68) and Homann (69). A more recent review concentrating on the effect of fuel type and the influence of aromatic fuels on soot formation has been given by Bittner and Howard (7). Using these reviews as a basis, some of the important aspects of soot formation can be discussed.

Briefly, soot formation can be broken down into three stages:

1. Soot particle nucleation
2. Formation of spherical units (about 250 Å)
by agglomeration and surface growth
3. Coagulation of spherical soot particles to
form the characteristic chain-like structure

While the above three stages are occurring, the soot particles also undergo dehydrogenation. The composition of the soot changes from about CH to C₈H (67), with trace amounts of oxygen, nitrogen, and other elements also present.

The first stage, soot particle nucleation, has probably been the most difficult to explain and consequently caused the most controversy. There is a lack of even qualitative information about how fuel molecules with only a few carbon atoms are transformed into even the smallest soot particles with some ten thousand carbon atoms (69). The two most viable hypotheses yet advanced are based on radical and ionic polymerizations (7). The ionic aspects of soot formation are especially important since virtually all explanations of the mode of action of metal-containing additives are at least partially based on the formation of metal ions in the flame, and their effect on the subsequent flame chemistry.

The theory that positive ions serve as the nucleus for carbon formation in flames (70,71) has been shown by Howard (72) to predict the well-known chained structure of carbon particles and the uniform size of the spherical chain units. A series of experiments by Howard and co-workers have proved the

feasibility of this theory. A mechanism for the ionic nucleation of soot particles has been described based on the experimental evidence (73). Positively charged agglomerates of carbon particles exhibiting a chained structure have been found with an average charge/particle ratio of about 2 (74). The size, size distribution, number concentration, and fraction of charged carbon particles has also been measured, and a coagulation rate constant obtained (75). The alkyl derivatives of PAH are believed to be the first precursors which may then grow by ionic or radical polymerization pathways (76, 77, 78) to high (> 500 amu) molecular weight species (79) of higher H/C ratio than the final soot. This material then agglomerates and dehydrogenates to form solid carbonaceous particulates (77, 80). The well-known PAH which can be extracted from soot particles (81) are believed to be the highly condensed and unreactive byproducts of this soot formation scheme (79,82).

Many of the proposed explanations as to how metal additives function to remove soot have included some sort of enhancement of the soot oxidation process. Therefore, a review of the knowledge concerning soot burnout in later flame zones is appropriate. Unfortunately, this process is also an area of mild controversy among researchers. The earliest work by Lee, Thring, and Beér (83) included an expression for the rate of soot burnout as a function of temperature and the partial pressure of O_2 . Millikan (84) and later Fenimore and Jones (85) found that soot was mainly oxidized by hydroxyl radicals, with only a weak dependence on O_2 partial pressure. They concluded that this effect was magnified under fuel-rich conditions, especially when H_2 was present as a source of radicals. More recently, Park and Appleton (86) and Feugier (87) have obtained rate expressions based on O_2 partial pressure. On the other hand, Blackwood and McTaggart (88) and Ates and Page (89) both support the theory of Fenimore and Jones that the predominant oxidative attack on the soot surface is by the hydroxyl radical. Thus, while it is impossible to make any universal statement, it seems clear that hydroxyl radicals are important, especially under fuel-rich conditions.

SECTION 4

LABORATORY FLAMES

4.1. OVERVIEW

The widely varying degrees of effectiveness of metal additives reported in reducing soot formation in practical combustors gives evidence of the complex mechanism(s) involved in their action. It appears that many flame parameters (flame type, burner design, flame temperature, fuel equivalence ratio, and type of fuel) and even smoke evaluation technique are capable of having significant influences on at least some of the various additives. Therefore, it seems unwise to view laboratory flame results with the hope of determining which additives are most effective, as it is doubtful that equivalent results would be obtained in a practical combustor. Rather, the value of laboratory flame studies rests upon the variety of relatively well specified (although not necessarily practical) conditions that have been tested, and on the potential of the results to help elucidate the mechanism by which the various additives function. Therefore, we will not try to present the quantitative rankings of effectiveness of additives often reported in laboratory studies (except as they pertain to the mechanism of action) as this type of result would only be superfluous when compared to the myriad of results of practical studies already reported.

4.2. MECHANISMS

Below is a brief overview of the three mechanisms by which additives seem to function in flames, followed by the more detailed results which support each of the three mechanisms.

Mechanism I (Na, K, Cs, Ba): This is an ionic mechanism which occurs with additives which ionize extensively in the flame. The resulting additive ions act on natural flame ions (both molecular and particulate) to decrease the nucleation or coagulation rate. The result is a decrease of the amount of soot formed, or a shift of the particle size distribution to smaller sizes which burn out more quickly.

Mechanism II (Ba, Ca, Sr): Additives which act by this mechanism undergo a homogeneous reaction with flame gases to produce hydroxyl radicals which rapidly remove soot or gaseous hydrocarbon soot precursors. This action appears to occur throughout the flame, with significant decreases in flame radiation in the early flame zones.

Mechanism III (Mn, Fe, Co, Ni): This mechanism, which only occurs to appreciable extents late in the flame (oxygen rich secondary zone), is an acceleration of the oxidation rate, possibly by an occlusion of the metal in the soot particle. No significant decrease in primary zone flame radiation is typically observed with this mechanism.

These mechanisms are by no means independent. Barium appears to function at appreciable rates by both mechanisms I and II. In reality, all metal additives probably act to some extent by Mechanism I, as they all increase the ion concentration in flames. The purpose of this division into three distinct mechanisms is simply to provide a framework for the discussion of additive functions. In turn the classification of functions can of course be useful in selecting the best additive for a specific type of combustion system, as well as for mixing various additives to achieve the largest possible soot reduction.

Mechanism I (Na, K, Cs, Ba)

This mechanism is largely applicable to group I of the Periodic Table. These elements are known for their low ionization potentials (Table 2) and lack of significant catalytic effects on the reaction of concern here.

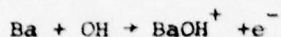
TABLE 2. IONIZATION POTENTIALS IN ELECTRON VOLTS (References 91-93 unless otherwise noted).

Li	5.39	Cr	6.76
Na	5.14	Mg	7.64
K	4.34	Ca	6.11
Cs	3.89	Sr	5.69
Fe	7.87	Ba	5.21
Co	7.86	Pb	7.42
Ni	7.63	Sn	7.34
Mn	7.43	Mo	7.10
Cu	7.72		
Zn	9.39		

Graphite ~ 4.35 (72)

Large Polycyclics ~ 7 - 10 (76)

Barium has also been shown to be capable of having significant activity by this mechanism (90), as it increases flame ionization levels in amounts similar to group I elements. This behavior is apparently due to the fact that it ionizes more readily than its ionization potential indicates, by chem-ionization reactions of the type (91):



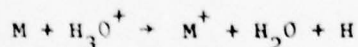
Calcium and strontium, which like barium are alkaline earths, apparently (90) do not contribute as many ions to the flame by this mechanism as barium does.

One of the two possible explanations for the particle size distribution shift has been proposed by Haynes, Jander, and Wagner (90). These workers conducted experiments using a combination of light scattering and extinction measurements (79,94) allowing particle size determinations down to about 50 Å. Relatively low additive concentrations of a few ppm introduced in an aqueous spray yielded flame metal concentrations of 10^{10} to 10^{13} ions/cm³. These concentrations only slightly reduced the total amount of soot collected, but caused a pronounced shift in the particle size distribution. Typical shifts, after about 30 msec in the premixed flame, were from $N \sim 10^9$ to 4×10^{10} particles/cm³ and $d = 500$ to 160 Å.

This shift was explained by Haynes et al. to be entirely a post-nucleation effect caused by a more rapid and complete ionization of the (incipient) soot particles. According to this explanation, the coagulation rate was reduced by the associated increase in the electrostatic repulsion between soot particles. Calculations by Haynes et al. over a variety of premixed flame conditions showed that this size distribution shift could be attributed to an order-of-magnitude decrease in the coagulation rate constant. Although the explanation fits the data, it is not clear how an additive of lower ionization potential than the soot particles can do other than remove charge from the latter (see below).

The second possible explanation for Mechanism I is based on the size distribution shift observed by Bulewicz, Evans, and Padley (95) in propane-oxygen diffusion flames. These authors also observed smaller size particles with additive use, but they reported a smaller number of particles whereas Haynes observed a larger number of particles.

Bulewicz et al. assume that the additive ions have a pronounced effect on the ionic nucleation mechanism. This theory is based on what would appear to be a rather well established fact that metal additives, while increasing the overall (metal plus hydrocarbon) ion concentration, actually decrease the concentration of natural flame ions (91, 92, 98) via charge transfer reactions of the type (92):



This decrease in natural flame hydrocarbon ions can be expected to decrease the rate of ionic nucleation (95), as metal ions are not suspected to be as efficient as nuclei for soot formation as are hydrocarbon ions (91,92).

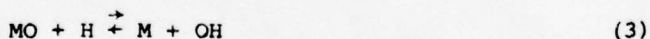
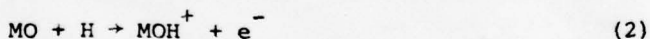
An additional observation by Bulewicz et al. (95) was that additives such as K and Cs exhibited pro-soot behavior at low concentrations ($< 10^{10}$ ions/cm³) and only at slightly higher concentrations yielded anti-soot effects. Feugier (96,97) observed this same effect in fuel-rich premixed, ethylene/air flames. However, while Bulewicz et al. explained both the pro-soot and anti-soot effects on an ionic basis, Feugier attributed only the pro-soot effect to ions, stating that the anti-soot effect was due to an effect on radicals similar to Mechanism II.

The different results observed by Haynes et al (90) and Bulewicz et al. (95) can perhaps be explained by considering the two different combustion systems involved. The oxygen-rich diffusion flame used by Bulewicz et al. could be expected to burn out small soot particles, resulting in both a smaller number of soot particles and a significant decrease in actual weight of soot collected, as were observed. In contrast, the fuel-rich, premixed flame of Haynes et al. would be oxygen-deficient in later flame zones where small soot particles could therefore persist. The results would be a larger number of smaller soot particles and little reduction in the weight of soot, as were observed.

Mechanism II (Ba, Ca, Sr)

This mechanism is based largely on the observations of Cotton, Friswell, and Jenkins (99,100) in propane diffusion flames. An important characteristic which distinguishes it from Mechanism III is its occurrence under fuel rich as well as fuel lean conditions, and therefore in primary as well as secondary flame zones.

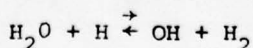
Schofield and Sugden (101) were apparently the first to investigate the formation of the alkaline earth hydroxide ions:



Jensen (102) later reported enthalpy changes and equilibrium constants for these reactions.

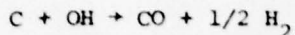
Cotton et al. (99) studied the effects of forty different metal additives and concluded that these additives reduce soot by at least two different mechanisms. The distinguishing characteristic was that the alkaline earths reduced soot (to same extent) at all fuel equivalence ratios studied, whereas the other metals only acted under lean combustion conditions.

Cotton et al. proposed that the effect of the above reactions, 1-3, was to keep reactions of the type



balanced in the luminous zone of a hydrocarbon flame. Thus the OH concentration was prevented from dropping below equilibrium (as it was assumed to be in the

absence of the metal additive) and hence an accelerated rate of carbon oxidation was achieved via



Haynes et al. (90) observed a similar distinction between the alkali metals and alkaline earths (Ba excepted). These metals demonstrated a strong ability to reduce soot formation, although no direct change in number density of soot particles was observed. These workers further asserted that Ca and Sr were not capable of generating enough ions to inhibit significantly the coagulation process (even with allowance for chemi-ionization and charge transfer). Consequently, they agreed in part with the mechanism proposed by Cotton et al., but they argued that even the maximum possible OH concentration could not account for the observed soot reduction if OH acted solely on the already condensed soot. They concluded that the main chemical mechanism must therefore be OH oxidation of the gaseous hydrocarbon soot precursors.

This mechanism has also gained support from some of the practical studies (already discussed) where the addition of Ba, Sr, or Ca results in a decrease in the measured wall temperature (15,16) due to more heat being retained in the flame. This wall temperature decrease is (rightfully) attributed to a decrease in flame radiation resulting from less soot being formed.

Ibiricu and Gaydon (103) have reported that halogen compounds inhibit flames by removal of OH radicals in a mechanism similar to the reverse of Mechanism II, namely



where X is a halogen atom. They hypothesized that this reaction promotes carbon formation which increases radiation losses and cools the flame, yielding higher measured wall temperatures.

Mechanism III (Mn, Fe, Co, Ni)

The exact mode of action of these additives is not well established, but can be attributed to yet a third mechanism. Use of these additives reduces the amount of soot formed with relatively minor size distribution changes (32,37). The distinct feature of these additives is that they only function appreciably in later flame zones, where soot oxidation occurs. Two of the most well-known commercial additives, MMT (Mn) and ferrocene (Fe), contain the transition metals which act by this mechanism.

Early evidence of this reaction mechanism comes from the work of Fenimore and Jones (85) on the oxidation of soot by hydroxyl radicals. They observed that Mn (in the form of MMT) had no effect on the amount of soot formed in a fuel-rich premixed $C_2H_2/O_2/Ar$ flame. However, in flame gases having appreciable oxygen, they observed about a 20% increase in the rate of reaction.

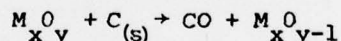
Fenimore and Jones also conducted experiments with soot samples containing 1% manganese by weight. They discovered that this Mn doped soot oxidized 120°C lower than soot which was free of manganese. The maximum rate occurred at 407°C for the Mn catalyzed soot. Nabel and Cramer (104) observed a strikingly similar result in their studies on the mechanism of action of ferrocene in smoke reduction. They reported (105) that ferrocene reduced the ignition temperature of

soot collected at the same height in a flame, from 585°C to 460°C; a 125°C reduction.

Practical studies by Friswell (15) and Shirmer (16,106) reported similar smoke reductions with Mn and Fe compounds. They also agreed that Ba yields a significant reduction in primary zone flame radiation, whereas neither Mn or Fe yielded noticeable reductions. Recent USAF studies (107) have also indicated that while Mn (MMT) substantially reduces soot in gas turbines, it has virtually no effect on combustor liner temperature. Meanwhile, gas turbine tests by Shaysen (11) of a barium fuel additive showed a substantial drop in flame radiation and temperature. It seems clear that Ba acts by a different mechanism (II) than Mn or Fe (III).

The inclusion of Co and Ni in the same group as Mn and Fe is based on somewhat scarce evidence. They have been shown to have some soot reducing capability (91, 17), and are all first row transition metals with similar electronic structure and chemical properties (108). Additionally, Addecott and Nutt (91) pointed out that not only did Mn and Co have similar smoke reduction capabilities in their studies, but they also produced virtually the same total ion concentration. Nickel was only slightly further away in ion concentration and smoke reduction.

Cotton, Friswell, and Jenkins (99) have speculated that Mechanism III works by occlusion of the metal in soot particles, which subsequently oxidize at an accelerated rate in oxygen rich flame zones. They also speculated that metal oxides are formed which then remove soot by a reaction such as



4.3. MATHEMATICAL MODELS

Several authors have attempted to correlate their quantitative soot reduction data using mathematical models. These attempts have most often been an empirical data reduction technique, as the theoretical basis for the additives' action was not considered to be well established.

Shirmer's report (16) of Bagnetto's experiments (9) included an empirical expression to relate the optical density (Von Brand Smoke units) of the exhaust gases to the inlet temperature and pressure of operation of the two-inch model gas turbine combustor:

$$\begin{aligned} \text{Optical Density} = & 3.404 \times 10^{-1} + 2.873 \times 10^{-2} P \\ & - 6.195 \times 10^{-1} T - 2.396 \times 10^{-1} PT + 2.625 \times 10^{-1} T^2 \end{aligned}$$

Another equation was also given for the optical density when the additive was employed:

$$\begin{aligned} \text{Optical Density} = & 2.634 \times 10^{-1} + 5.943 \times 10^{-3} P - \\ & - 6.817 \times 10^{-1} T - 9.947 \times 10^{-2} PT + 4.614 \times 10^{-1} T^2 \end{aligned}$$

The concentration of the additive was unfortunately not included as a variable, and apparently a different equation would be necessary for each of the three additive concentrations tested. The fact that the equation contained five empirical constants also diminishes its significance slightly.

Plonsker and coworkers (32) have obtained a somewhat better empirical correlation using only two constants (A,k):

$$\log_e S = A - kx$$

where x is the additive concentration in ppm and S is some measure of the smoke concentration [Bacharach Smoke number, or (100 - Von Brand Smoke reading)]. These authors obtained good agreement with their data, but unfortunately found it necessary to use different constants for each of the three gas turbines they tested, as well as each of the various load conditions.

Champagne (33) has developed at least a partially theoretical expression for Plonsker's data (32), based on a very general thermal and catalytic approach for the burnout of carbon. The final expression obtained is

$$\Delta C = \frac{k_1 [Mn]}{k_2 [Mn] + k_3}$$

where ΔC is the carbon reduction due to the Mn additive, $[Mn]$ is the concentration of additive in the fuel as MMT, and $k_1 - k_3$ are constants. Champagne's result is valid only under constant load conditions, and also requires new constants for each of the three turbines. Additionally, Champagne's three-constant theoretical expression did not appear to fit the data as well as Plonsker's two constant empirical relation.

Novakov et al. (31) found that the power law

$$n(r) = Cr^{-b}$$

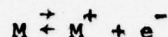
where b and C are constants, was able to describe the particle size distribution shift which they observed when using a manganese fuel additive. The agreement was fair, although there was a good deal of scatter in the experimental data.

Feugier (96,97) developed several semi-empirical models, starting from the broad theoretical base that all soot precursors, P , are either oxidized (with rate V_1) or nucleated to small soot particles (with rate V_2).

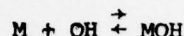
For Cs, K, and Na, the final expression obtained is

$$\left\{ \frac{y}{\left(\frac{V_1}{V_2} \right) - y} \right\} \left\{ \frac{1 + \left(\frac{V_1}{V_2} \right)}{[K/(1 + \phi)]^{1/2}} \right\} = \gamma \alpha (Mo)^{1/2}$$

where M_0 is the total molar fraction of metal in the flame; K is the equilibrium constant of the reaction



and ϕ is $(OH)_{eq}/K'$ where K' is the equilibrium constant of the reaction



Values for K , K' , and equilibrium hydroxide concentrations $(OH)_{eq}$ were obtained from data in the literature. The product $\gamma\alpha$ is an empirical constant, as is the ratio (V_1/V_2) . The variable y includes the soot reduction ratio x/x_0 (soot with the additive/soot without the additive) plus yet a third empirical constant. The agreement of this expression with Feugier's data is fair.

For Li and the alkaline earth metals the expression obtained by Feugier is:

$$\left(\frac{x_0}{x} - 1\right) = \frac{\mu m}{V_1 + V_2} = \frac{\mu \delta Meq}{V_1 + V_2}$$

where μ and δ are empirical constants, as is the sum $(V_1 + V_2)$. M is the mean molar fraction of free metal in the carbon formation zone, and Meq is the mean molar fraction of free metal at thermodynamic equilibrium at the same temperature (obtained from literature data). The agreement with Feugier's data is not quite as good here as with Cs, K, and Na.

One interesting technique employed by Feugier was to separate his results according to the suspected different mechanisms of action of groups I and II of the periodic table. Further modelling work should probably also take this approach. This would allow size distribution shifts (important to Mechanism I), such as those modelled by Novakov (31), to be incorporated when necessary. Hydroxide thermodynamic data, as obtained by Jensen (100), could be used in a Mechanism II model along with the rate expressions for carbon burnout in the presence of additives reported by Cotton et al. (99). Possibly even other theoretical parameters would be necessary for the as yet uncertain Mechanism III.

4.4. ADDITIONAL METAL ADDITIVES

Several metals in addition to those already listed have also been tested for their ability to reduce soot formation in flames. These metals are typically not known for their effectiveness, and consequently have not been as extensively tested. The dominant mechanism by which they act is usually still unknown.

Lithium has been shown by Addecott and Nutt (91) to yield positive ion concentration in flames similar to other Mechanism I metals. On the other hand, lithium has been shown by Bulewicz and Padley (109) to form hydroxides similar to Mechanism II metals.

Using premixed hydrogen/air flames, Bulewicz and Padley (109) have also

shown that Mg, Cr, Sn, and U all form hydroxides and probably function by Mechanism II. Cotton, Friswell, and Jenkins (99) also included Mo with Mechanism II metals, reporting it to be more effective than Ca and Sr at soot removal in propane diffusion flames.

Addecott and Nutt (91) reported smoke reductions for Pb, Cu, and Zr similar to the transition metals Ni and Co, while Cotton et al. (99) found all of these metals to be ineffective.

4.5. FORM OF METAL ADDITIVES

Several laboratory-scale experimenters have addressed the question of effects due to the form in which the metal is added to the flame. Salooja (98) tested different salts of Ba and found that they all acted the same as BaO. Addecott and Nutt (91) reached similar conclusions.

Bulewicz and Padley (109) have pointed out that volatile compounds [such as $\text{Sn}(\text{CH}_3)_4$] may cause less catalysis than a spray additive of a Sn salt.

Organometallic compounds are usually employed to increase the solubility of the metal in a petroleum fuel. Air Force studies (42) summarized by Blazowski (41) showed no effect of the organic ligand. However, ferrocene is known (108) for its extreme thermal stability (to $>500^\circ\text{C}$), and thus in some flames the dicyclopentadienyl compounds may not have any significant catalytic effect until the high temperature zones.

4.6. ROLE OF ELECTRONS

Salooja (98,110) and Weinberg (111) have conducted experiments with metal oxide coated wires in diffusion flames. They have observed strong anti-sooting effects when the wires are inserted in the primary reaction zone at the base of the flame, and pro-sooting effects when the wires are inserted in the later pyrolysis zones. Weinberg has explained these results on the basis of the free electrons that these easily ionizing wires contribute to the flame.

According to Weinberg (111), the maximum rate of agglomeration of particles will occur when half are charged and half uncharged. (This statement is only true as a first approximation, that is, when the consideration of interparticle forces is limited to electrostatic repulsion between charged particles. When the analysis includes attractive forces between charged and neutral particles, that is, image forces arising from induced charge, it is found that the maximum rate may occur with significantly less than half of the particles charged.) Thus, early in the flame when there are many particles and only a small proportion charged, the electrons neutralize even more particles, reducing the rate of agglomeration and yielding an anti-soot effect. Later in the flame when there are fewer (and larger) particles, and almost all of them are charged, the electrons will again provide more neutral species, which will now result in an increased rate of agglomeration, and the corresponding pro-soot effect. The observed change in size of the luminous zone of the flame is due to the longer burnout time required with the larger particles.

In contrast to the foregoing, Haynes et al. (90) reported that in premixed flames electrons did not play a significant role in the action of the additive. This conclusion was based on the use of electric fields to pull electrons out of the flame. A potential of only -300 to +300 volts was used, but the exact field strength was not stated. If the distances were large enough, it is possible that the field was not strong enough to pull electrons out of the flame.

Even if electrons are not important in premixed flames, Haynes et al. (90) pointed out that this may not be true for diffusion flames where the lean oxidation zone contains few hydrocarbons to trap electrons.

Many practical flames of interest are turbulent diffusion systems which have aspects of both premixed and diffusion flames. It is therefore difficult to state, a priori, what effect an influx of electrons would have at various points in a turbulent diffusion system. The possibility for soot control by this approach deserves further investigation since it would not contribute harmful metal additives to the exhaust.

SECTION 5

CONCLUSIONS

Metal additives have been amply demonstrated to reduce the soot content in the exhaust of practical flames. Generally, the most effective additives are those which contain Mn, Fe, or Ba. The additives typically achieve the most noticeable reductions in soot under heavily sooting conditions - high power, high load, or poorly maintained combustors. Systems with relatively clean exhaust often exhibit an increase in particulate emission due to metal oxides from the additive.

The metal oxide particulates resulting from additive usage are relatively non-toxic in the case of Fe, slightly toxic in the case of Ba, and possibly very toxic in the case of Mn. However, the health effects of all additives (especially manganese) deserve further attention, since it is possible that some of them may constitute a greater health hazard to the public than does the soot they remove.

The mechanism by which metals from groups I and II of the periodic table function is more firmly established than is the mechanism by which the transition metals act. However, the understanding of the role of any of the additives is qualitative. The mechanism of action of the highly effective transition metals should be investigated in well-defined laboratory flames. A better understanding of this mechanism would be very useful, especially in the formulation of additive combinations. The prevailing disagreement between the experiments of Bulewicz and Padley (109) and Haynes et al. (90) as to whether alkali metals affect the soot nucleation step should be resolved in laboratory experiments permitting simultaneous measurement of soot particle number concentration and particle size distribution.

The mechanisms by which additives are believed to act suggests that a carefully selected combination of additives might achieve greater results than any one additive separately. Variations in combustion system temperature could also be at least partially compensated for by the use of such a combination of additives. For example, Cotton et al. (99) report that Ba and Mn have similar efficiencies at 1500 - 1600°K, whereas Ba is much more effective at 2000°K. Additive combinations could also be used to overcome problems of decreased fuel thermal stability, caused by only one additive, and metal oxide deposition on combustor surfaces (41). Consequently, various additive combinations certainly deserve further attention.

Combustor design modifications are generally the preferred long-term solution to sooting problems. Metal additives should only be considered for short term use, or where design modifications are unacceptable.

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