

**EFFECTS OF FUEL ADDITIVES  
ON AIR POLLUTANT EMISSIONS  
FROM  
DISTILLATE-OIL-FIRED FURNACES**



**U. S. ENVIRONMENTAL PROTECTION AGENCY**

# **EFFECTS OF FUEL ADDITIVES ON AIR POLLUTANT EMISSIONS FROM DISTILLATE-OIL-FIRED FURNACES**

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## ABSTRACT

The Office of Air Programs of the U.S. Environmental Protection Agency has recently completed a study of the use of fuel additives to control air pollution from distillate oil burning systems. The available literature was surveyed, and samples of all known additives procured. Each additive was analyzed for elemental composition to provide a basis for testing. A standard screening procedure was established to test the effect of each additive on emissions from fuel oil combustion. Screening tests were carried out on all distillate soluble additives. The most promising additives were then subjected to a rigorous examination. This report is a comprehensive summary of the entire program.

The results show that fuel additives are not a promising way of reducing air pollution from distillate oil combustion. A majority of the additives tested had no beneficial effects on air pollutant emissions; in fact, some additives even increased total particulate and  $\text{NO}_x$  emissions. Several of the metal-containing additives, e.g., Ferrocene, CI-2, and Fuelco  $\text{SO}_3$ , reduced total particulate emissions; however, the unknown toxicity of new emissions they create makes their use questionable. Further, there is evidence that for distillate oils, burner modifications are a more suitable route to air pollution control.

# **EFFECTS OF FUEL ADDITIVES ON AIR POLLUTANT EMISSIONS FROM DISTILLATE-OIL-FIRED FURNACES**

## **INTRODUCTION**

### **HISTORY**

This investigation of the relationship of fuel additive technology to air pollution control was begun with a literature survey and contacts with individuals knowledgeable in the use of additives for specific situations. Additives for all fuels except coal and gasoline were considered. The published literature revealed little information on the effects of fuel additives in reducing, increasing, or creating emissions of air pollutants. Contacts with the oil industry revealed that proprietary work had been done in certain areas (primarily with combustion improvers), but the information was not generally available. Publications collected after the initial literature survey only provided more information on manufacturers' claims of additive effects. In this work all available distillate soluble additives were examined. Many fuel additives are designed for functions not related to combustion (for example, as dispersants) and, therefore, have little direct effect on reduction of air pollution. These compounds may, however, add new types of air pollutants, such as metals, to the environment and were, therefore, included in the testing program.

This document is a final report on the investigation by the Air Pollution Control Office of the U.S. Environmental Protection Agency into the use of fuel additives as a means of reducing air pollutant emissions from the combustion of distillate fuel oil. Mention of company and product names herein does not constitute endorsement by the U.S. Environmental Protection Agency.

### **PURPOSE**

This study was the first phase of a program to explore the possibility of using additives to reduce the air pollution from fuel oil combustion. In this phase additives for distillate oil were examined.

Questions to be answered by this study included the following: What are the effects of additives on emissions of air pollutants from combustion processes? What additive concentrations are the most effective in reducing the amount of emissions? Are those additives that are effective also practical in terms of cost, toxicity, corrosion, and fuel and additive stability?

## SUMMARY

The results of this study show that in distillate oil most fuel additives have no beneficial effects on the air pollution problem. Fewer than 10 percent of the additives tested produced any pollutant reduction, whereas more than 20 percent increased emissions of at least one pollutant. In a few cases proprietary metallic additives substantially reduced particulate emissions, but in no case did an additive reduce the emissions of carbon monoxide, unburned hydrocarbons, sulfur oxides, or nitrogen oxides.

From a cost/effectiveness viewpoint Ferrocene (Arapahoe Chemicals) and CI-2 (Ethyl Corp.) have the greatest impact on total particulate emissions. CI-2 added to the distillate oil for a residential heating unit at a cost of about \$2.00 per year could reduce particulate emissions 40 percent. Unfortunately, however, both Ferrocene and CI-2 contain large amounts of metals; Ferrocene is 20 percent iron, and CI-2 is 20 percent manganese. This causes a high concentration of metal compounds in the flue gas, and the possible toxicity of these new emissions makes the use of additives very questionable. Further, properly designed flame retention devices can be easily added to standard oil burners to produce greater reductions in particulate emissions than any additive tested. Since such flame retention devices provide greater reductions of particulate emissions, present no toxicity problems, and are currently available at a cost of only about \$25.00, it is recommended that none of the fuel additives tested be used as a means of controlling air pollutant emissions from distillate oil burning.

# EXPERIMENTAL APPROACH

## ADDITIVES

With the cooperation of many manufacturers, samples of some 206 additives were collected for testing. Appendix A contains a listing of these additives, along with company name for each, suggested fuel dose (concentration), function and general composition. Names and addresses of manufacturers are given in Appendix B. The additives collected were intended for use in a variety of fuels. The major fuel types represented are distillate oil (No. 1 and No. 2), heavy distillate (No. 4 and No. 5), residual oil (No. 6 and Bunker C), and coal. Distillate oils also include kerosene and diesel fuel. In this work all additives that were soluble in distillate oil were tested even though many of them were not recommended for use in distillate oil. This policy was formulated to ensure completeness of the testing program and will be maintained in the upcoming testing of the use of additives in a residual oil burner.

Most commercial additives are designated as performing certain functions in the fuel. These functions are listed alphabetically (with synonyms) below:

1. Chelating agent (metal deactivator).
2. Combustion improver (combustion catalyst).
3. Corrosion inhibitor (rust inhibitor, acid neutralizer, oxidation inhibitor, antioxidant).
4. Demulsifying agent (antihaze).
5. Dispersant (emulsifier, surface active agent, detergent).
6. Gum inhibitor (antifouling agent).
7. Odor maskants.
8. Pour point depressant (cold flow improver).
9. Stabilizer (color stabilizer).

Additives intended to fulfill several of these functions are usually advertised as multipurpose additives.

## TEST PLAN

The experimental phase of the evaluation included characterizing the chemical composition of the additive compounds and measuring their effects on emissions of air pollutants. While these additive samples and related literature were being collected and analyzed, the oil-fired test systems was constructed, instrumented, and operated with a standard No. 2 fuel oil to establish baseline operating performance over a range of air-fuel ratios.<sup>1,2</sup> Flue gas from the test system was analyzed for particulate matter, smoke, carbon monoxide, carbon dioxide, oxygen, total gaseous hydrocarbons, oxides of nitrogen, and



oxides of sulfur. An operating air-fuel ratio that produced a moderate amount of particulate matter (0.14 to 0.20 gram per kilogram of fuel) in the flue gas was chosen for screening the additives. Additives effects were evaluated by comparing emissions with additives with baseline performance data.

The additives tested were commercially available, proprietary formulations. Since knowledge of the elemental composition of the proprietary additives was required, each product was analyzed for elemental constituents by an independent laboratory. Based on analysis the additives were then sub-categorized either as metallic or non-metallic and a uniform dose rate established. In cases wherein the measured composition varied from the manufacturers claims, the measured values were used. Additives that showed promise in this screening study were evaluated more thoroughly at a variety of concentrations.

# TEST FACILITY

## FURNACE DESIGN

The experimental furnace is illustrated in Figure 1. Schematics of the test facility are shown in Figures 2 and 3. The combustion chamber design provides a residence time of 0.60 second at 20 percent excess air. (Typical residence times are 0.36 second at 20 percent excess air for a residential furnace burning No. 2 oil and 1.5 to 2.0 seconds for larger boilers.) The experimental furnace has a standard high-pressure atomizing gunburner that feeds fuel at a rate of 1.0 gallon per hour through an 80-degree hollow cone nozzle. The air-cooled,

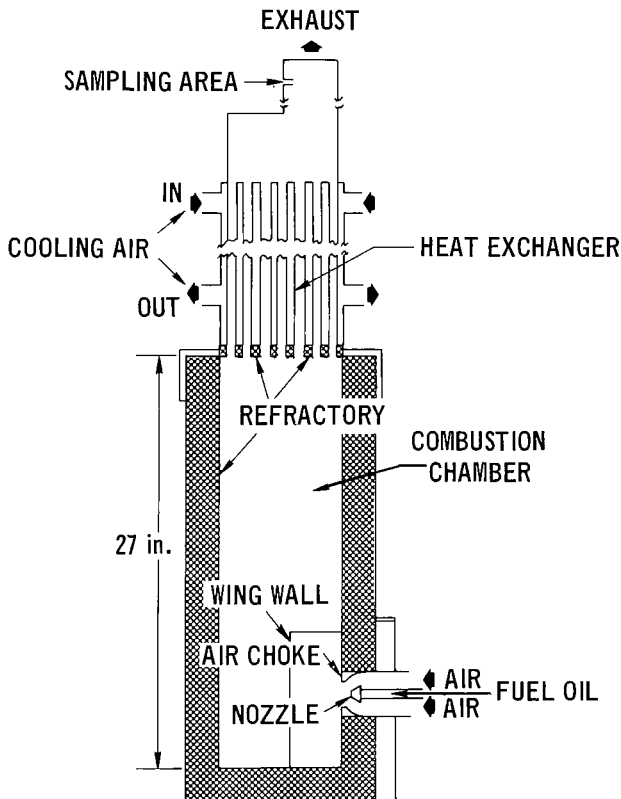


Figure 1. Experimental furnace interior detail.

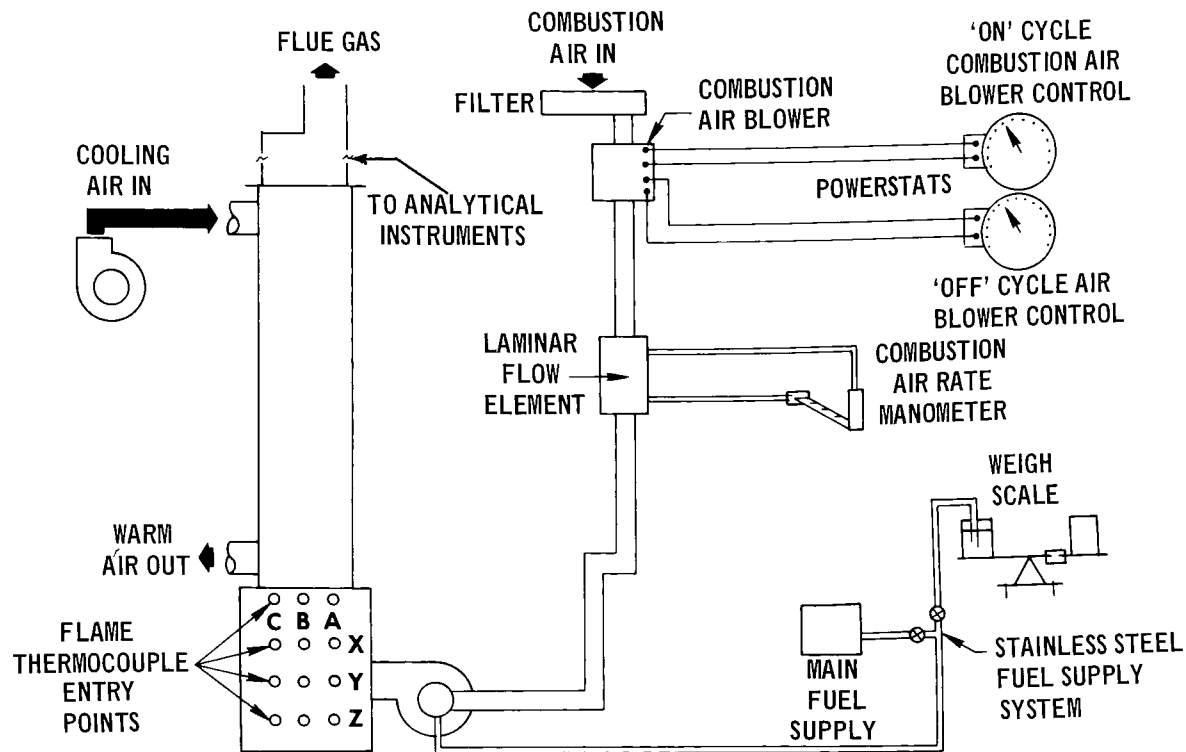


Figure 2. Experimental furnace schematic.

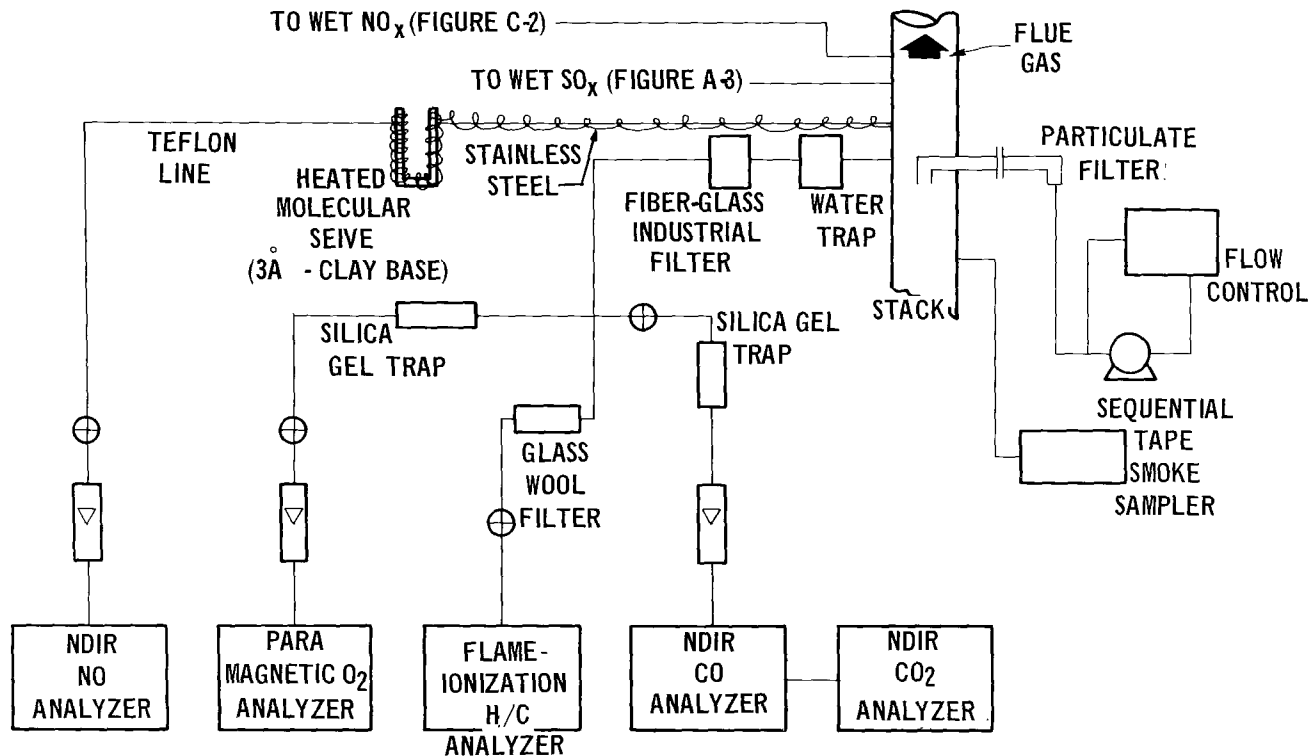


Figure 3. Analytical system.

steel heat exchanger is a shell-and-tube type with combustion gases on the tube side. A baffled stack provides a homogeneous gas mixture for sampling. Combustion air is measured with a laminar flow element and regulated by a blower controlled by a powerstat to produce the designated excess air level. Fuel weight is determined by mounting the fuel tank on a scale.

## TEST CYCLE

The furnace was operated on an average of 10 minutes "on" followed by 20 minutes "off." This cycle was chosen to allow investigation of the effects of startup and shutdown interactions on emissions. During the burner-off period, an auxiliary powerstat regulated the blower to provide a reduced flow of air into the furnace for heat removal and pollutant sampling. A programmed cam timer regulated this cyclic operation. For reporting purposes, each "burner-on" period was defined as a "run."

## STANDARD FUEL

To provide uniform test fuel with a low background of metal contaminants, a large quantity of a No. 2 oil was obtained and stored under a pure nitrogen blanket. This distillate oil was from a Gulf Coast crude stock, containing a mixture of straight distilled and cat-cracked products. API gravity was  $36^{\circ}$ ; aromatic content, 25 percent; sulfur content, 0.1 percent; nitrogen content, 0.01 percent; and mass ratio of carbon to hydrogen, 6.62:1 (molecular formula  $\text{CH}_{1.81}$ ).

## ANALYTICAL PROCEDURES

Sampling and analytical procedures were identical to those used in earlier studies by Martin and Wasser<sup>1,2</sup>: paramagnetic oxygen analysis, flame ionization detection for unburned hydrocarbons, nondispersive infrared for carbon monoxide and dioxide, sequential smoke sampler, Combustion Engineering-Shell method for sulfur oxides, phenol disulfonic acid method for oxides of nitrogen, and collection of filterable and condensable particulate. A detailed discussion of these procedures is provided in Appendix C. In a modified method, a woven silver filter was used to collect filterable particulate matter from selected runs to simplify chemical analysis of the particulate matter. Solid particulate matter was analyzed for metals content and ultimate constituents (C, H, N, S, and O) to determine changes in composition caused by the additive. Condensable particulate matter was collected on selected runs where it was necessary to quantify a specific additive element.

# TEST PROCEDURE

## ADDITIVE CONCENTRATION

One factor that had to be established was the range of additive-to-fuel ratios that would be effective in reducing air pollutants. Each manufacturer specifies the concentration for his particular additive; however, for the purposes of comparison it is often desirable to base the concentration on some component of the additive, such as a certain metal or organic specie. The approaches used in this study are outlined below.

In most cases where the additive contained a large amount of metal ( $>0.1$  wt %), two methods were used to determine the test concentration. First, the additive was tested at the level specified by the manufacturer. Second, it was tested at a concentration set on a standard basis involving the metal content of the additive. The data of Riggs<sup>3</sup> were used to select a metal concentration of 0.5 millimole of metal per kilogram of fuel as an appropriate starting point for evaluating effects on particulates. This level of metal in the fuel also results in a reasonable level of metallic emissions, at least as compared with the overall mass of the particulate. In this study, all metals present in the additive were summed as the basis for arriving at 0.5 millimole metal per kilogram of fuel. The differences in concentration that result from use of these methods depend on the amount and type of metal in the additive. Normally manufacturers' suggested concentrations range from 1:1000 to 1:8000 for a metal content greater than 0.1 weight percent. The potential variation in concentration based on the moles of metal is 1:1000 to 1:25,000. If the "standard" concentration was different from the one recommended by the manufacturer by more than a factor of 4, the additive was tested at both concentrations.

Note that most of the additives that contain less than 0.1 weight percent metal would require an additive concentration greater than 1 percent by weight to produce the 0.5-millimole level. From a purely economic standpoint these additives were grouped as non-metals.

The available literature did not indicate any method for choosing a standard concentration for non-metallic additives. One method considered involved basing the additive concentration on the elemental composition, specifically oxygen, nitrogen, sulfur, and halogen. This method was not selected because it related only to potentially detrimental effects, e.g., increased pollutant emissions due to conversion of additive constituents to  $\text{NO}_x$ ,  $\text{SO}_x$ , or  $\text{HCl}$ , or inhibition of combustion by halogens. The method chosen was to base the test concentration on the manufacturer's recommendation.

## AIR-TO-FUEL RATIO

To eliminate the effect of excess air variation on pollutant emissions, all tests were conducted at the same air-fuel ratio. The ratio was chosen to duplicate operation of a furnace at a marginal condition from the standpoint of particulate and smoke emissions (0.14 to 0.20 gram per kilogram of fuel). This loading was chosen so that enough material would be provided for accurate determination of additive-related changes in soot and for accurate chemical analysis without creating a soot-fouling problem in the furnace. For the test furnace the air-fuel ratio chosen was approximately 1.2 times stoichiometric, i.e., a ratio that would provide 20 percent excess air.

## ADDITIVE TESTING

### Test Series

A complete test consisted of 15 half-hour cycles or runs. Oxygen, gaseous hydrocarbon, carbon monoxide, and carbon dioxide were determined continuously; oxides of nitrogen and sulfur were determined on six cycles; and particulate emissions, on selected cycles.

### Additive Tests

For an additive test series, the furnace was brought to operating equilibrium by burning blank oil for six cycles. The next cycle was defined as a "blank run," during which pollutant data were collected. The fuel supply was switched to one containing the additive, and one purge cycle was used to clear the fuel line and burner of blank oil. The additive test consisted of the next 10 cycles. Tests were completed with a purge cycle and two blank cycles.

The monitoring instruments recorded data continuously on all cycles. Oxides of nitrogen and sulfur were determined on four additive cycles spaced to cover the entire test period and on two blank cycles, one in the morning, and the other in the afternoon. Particulate matter was collected on all cycles, and the weight of filterable particulate was determined. The silver filters were used on two blank cycles and three additive cycles. Fuel weights were taken, and excess air was controlled for all blank and additive cycles.

### Background Checks

To check the operation of the furnace, background runs were made periodically with the standard fuel oil (blank) through all 15 cycles. Data were compared with baseline data previously collected to detect any change in furnace operation.

# RESULTS

## COMPLETE TABULATION

The numbers in the second column of Appendix A denote the additives that were tested in distillate oil. Moreover, these numbers have been used to index the complete tabulation of all results in Appendix D. For each additive, this appendix shows the concentrations tested, the resulting effect on emissions, and the chemical analysis of the additive. Each emission number (columns 3-6) is the ratio of emissions with the additive in the fuel to emissions without the additive (i.e., emissions from the pure fuel). A ratio less than 1.0 represents an improvement of performance attributable to the additive.

## CONFIDENCE LIMITS

To ensure a completely fair evaluation program, several precautions were taken. First, in an effort to preclude any day-to-day variations in furnace operation, the performance of each additive was based on the data from standard fuel runs on that particular day. Further, all-day pure fuel tests were made periodically throughout the entire program to check burner performance. A detailed statistical analysis revealed that the following standard deviations were inherent within the system: particulate ratios  $\pm 7$  percent,  $\text{SO}_x$  ratios  $\pm 3$  percent, and  $\text{NO}_x$  ratios  $\pm 7$  percent. Thus, there is 95 percent certainty that a ratio less than 0.85 is significant.

## CARBON DIOXIDE AND OXYGEN

The amount of carbon dioxide produced by burning a given weight of fuel can be calculated from a stoichiometric equation based on the composition of the fuel. The amount of oxygen required can be determined in a similar manner; and, therefore, the exit oxygen level can be calculated. Throughout the entire work the measured concentrations of  $\text{CO}_2$  and  $\text{O}_2$  were extremely close to the theoretically calculated ones. That is, no additive had any noticeable effect on the efficiency of combustion.

## CARBON MONOXIDE AND HYDROCARBONS

Carbon monoxide and unburned hydrocarbons are emitted in flue gas in accordance with the concentration-time patterns shown in Figure 4. When the burner first fires, an emission peak is caused by the relatively cold firebox.



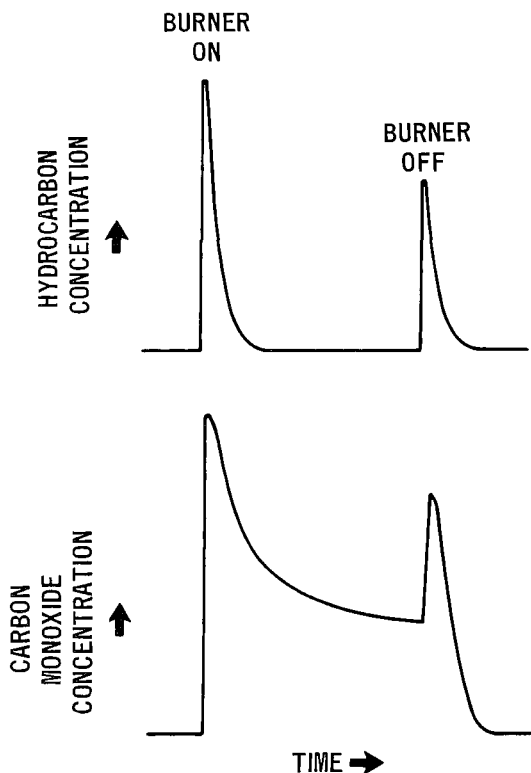


Figure 4. Startup and shutdown effects on hydrocarbon and carbon monoxide concentration patterns.

Emissions then decrease to an equilibrium level (zero in the case of the hydrocarbons) during the firing cycle. After burner shutoff, a second peak is caused by partial oxidation of heated fuel dripping through the nozzle to the hot firebox. The nature of initial and final peak emissions appears to preclude any reduction of these emissions as a result of using additives. The equilibrium emission level in the CO curve was not reduced by any additive tested, nor were the peak values for CO and hydrocarbons affected by any additive tested.

## OXIDES OF SULFUR

The sulfur in the fuel is oxidized to produce sulfur dioxide and sulfur trioxide. In emissions from the test furnace, the sulfur trioxide concentration was less than 0.5 ppm and the sulfur dioxide averaged about 45 ppm, representing approximately 6 ppm less than the theoretical  $\text{SO}_2$  concentration calculated from the sulfur in the fuel. None of the additives tested appeared to produce an effect on either of the sulfur oxide emissions.

## OXIDES OF NITROGEN

Emissions of oxides of nitrogen are attributable to two sources, isothermal fixation of atmospheric nitrogen at high temperatures and oxidation of nitrogen in the fuel or the additive. No additive tested decreased nitrogen oxide emissions; however, in a few cases  $\text{NO}_x$  emissions were increased as a result of oxidation of nitrogen contained in the additives.

## PARTICULATE MATTER

Another product of incomplete combustion is particulate matter, primarily carbon soot formed by thermal cracking of the fuel hydrocarbons. The greatest additive effects were expected and realized with this pollutant.

Columns 3 and 4 in Appendix D show the effect each additive had on particulate emissions. Total particulate refers to the total amount of solid material collected from the flue gas. Carbon particulate is the amount of carbon in the total material collected. In the case of pure fuel, these numbers are the same because chemical analyses revealed that essentially all of the particulate matter is carbon; however, with some additives, a noticeable amount of metallic oxide was collected causing a difference in the two weights and therefore in their respective emission ratios.

About 10 percent of the proprietary additives tested reduced total particulate, whereas nearly 20 percent increased total particulate to some extent. The particulate collected was analyzed for metals content, and the results were compared with the metals content of the additive. The apparent recovery of metals from the additives ranged from 15 to 100 percent.

# DISCUSSION OF RESULTS

## METALLIC ADDITIVES

The chemical analyses of the additives (Appendix D) revealed that almost half had a total metal content greater than 0.1 percent. Based on information in the literature, probable forms are: organo-metallics, Metallic sulfonates, and metal oxide slurries. These compounds represent a total of 14 different metals; however, only additives containing at least one of the transition metals; iron, manganese, or cobalt significantly reduced particulate emissions. Table 1 shows

**Table 1. DISTILLATE FUEL-OIL ADDITIVES THAT SUBSTANTIALLY REDUCED TOTAL PARTICULATE EMISSIONS**

Additive	Concentration		Composition	Total particulate ratio
	Weight	Molar <sup>a</sup>		
Arapahoe Ferrocene	1:7150	0.50	20% Fe	0.53
Ethyl Cl-2	1:9000	0.36	18.0% Mn	0.56
Commercial Chemical Improsoot	1:150	0.50	0.3% Ca 0.1% Ca	0.57
Gamlen DP 231	1:110	0.50	0.2% Mn 0.1% Fe	0.61
Fuel Combustion Corp. Fuelco SO <sub>3</sub>	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

<sup>a</sup>Millimoles per kilogram.

the seven most outstanding additives in distillate oil. Once the field was narrowed to these seven additives, concentration studies were conducted. Each of the additives was tested over a wide range of concentrations to determine an optimum concentration for particulate reduction. Figure 5 is a plot of particulate emissions versus concentration for CI-2 and is typical of all the results. Total particulate emissions decreased with increasing additive concentration up to a point. Beyond this point, the carbon particulate often continued to decrease, but total particulate emissions increased as a result of the increasing concentration of additive metal. As Table 1 shows, the optimum weight concentration is highly dependent upon the specific additive; however, it is interesting that each of the four most effective additives was most effective at a total metal concentration of 0.5 millimole per kilogram. This suggests a common chemical mass action mechanism.

The cost of using each additive was another important consideration in assessing the potential of fuel additives for reduction of pollutant emissions. Table 2 shows the smallest amount of each additive necessary to treat 10,000 gallons of distillate fuel oil and achieve a 35 percent reduction of particulate emissions. The cost figures are based on the best numbers available for additives in 500-pound lots f.o.b. the point of supply. This table points out very clearly that a purely economic point of view would favor Ferrocene, CI-2, and Fuelco  $\text{SO}_3$ . Further, it shows that using fuel additives is not extremely expensive, since it would take the average residential user between 10 and 20 years to burn

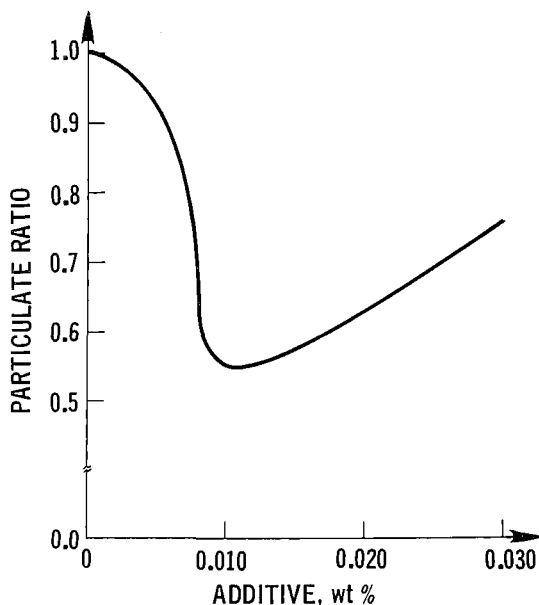


Figure 5. Particulate reduction versus CI 2 additive concentration.

**Table 2. COST OF TREATING 10,000 GALLONS OF FUEL OIL TO GIVE 35 PERCENT REDUCTION IN PARTICULATE EMISSIONS**

Additive	Amount needed, lb	Approximate cost, \$
Arapahoe Ferrocene	6	36
Ethyl CI-2	8	17
Commercial Chemical Improsoot	350	125
Gamlen DP 231	640	200
Fuel Combustion Corp. Fuelco SO <sub>3</sub>	95	34
Commercial Chemical Formula LSD	350	100
Industrial Chemicals Watcon 130	140	60

10,000 gallons of fuel oil, e.g., using CI-2 would cost less than \$2.00 per year. From a cost-effectiveness viewpoint Ferrocene and CI-2, are outstanding; however, if an additive is to be truly beneficial for control of air pollution, it must not add pollutants to the atmosphere.

Fortunately, the chemical structure of neither Ferrocene nor CI-2 is confidential.<sup>4,5</sup> Ferrocene is dicyclopentadienyl iron, and CI-2 contains methylcyclopentadienyl manganese tricarbonyl. Both compounds are sandwich transition metal complexes.

A preliminary toxicological investigation revealed that cyclopentadienyl manganese tricarbonyl is toxic at low concentrations and has marked cumulative properties.<sup>6</sup> Little specific information is available on dicyclopentadienyl iron; however, animal feeding experiments have shown an almost complete absence of toxicity.<sup>7</sup> These facts make Ferrocene more desirable from the standpoint of handling.

From an air pollution viewpoint the form of the metals emitted is important. An analysis of the particulate forms emitted revealed that in nearly all cases metals in additives are emitted as metal oxides. Table 3 shows the amounts of metal and metal oxide emissions that result from using nine different additives. Unfortunately, use of either Ferrocene or CI-2 causes a high metal concentration in the flue gas. Although the iron oxides from Ferrocene do not appear to be highly toxic (7), they do catalyze certain undesirable SO<sub>2</sub> reactions. Data indicate that manganese emissions are hazardous in themselves<sup>8</sup> and probably should be avoided.

Table 3. METAL EMISSIONS RESULTING FROM USE OF VARIOUS ADDITIVES

Additive	Dose	Composition	Metal emissions, <sup>a</sup> μg/m <sup>3</sup>	Metal emissions, <sup>a</sup> mg/kg fuel	Metal oxide <sup>b</sup> emissions, mg/kg fuel
Improsoot	1:150	0.3% Co 0.1% Ca	1,219 Co 406 Ca	20.0 Co 6.7 Ca	25.4 Co O 8.4 Cu O
Formula LSD	1:200	0.9% Co	2,744 Co	45.0 Co	57.0 Co O
Ferrocene	1:7150	20 % Fe	1,706 Fe	28.0 Fe	40.0 Fe <sub>2</sub> O <sub>3</sub>
Ethyl CI-2	1:9000	18.0% Mn	1,219 Mn	20.0 Mn	31.6 MnO <sub>2</sub>
Fuel CO SO <sub>3</sub>	1:750	0.25% Mn	300 Mn	3.3 Mn	5.2 MnO <sub>2</sub>
Gamlen DP 231	1:111	0.2% Mn 0.1% Fe	1,108 Mn 554 Fe	13.3 Mn 6.7 Fe	21.0 MnO <sub>2</sub> 9.6 Fe <sub>2</sub> O <sub>3</sub>
Watcon 130	1:500	0.15% Fe	831 Fe	3.0 Fe	4.3 Fe <sub>2</sub> O <sub>3</sub>

<sup>a</sup>This column shows the amount of metal emitted, probably in the form of an oxide.

<sup>b</sup>A standard burner emits about 200 milligrams of carbon particulate per kilogram of fuel burned.

## NON-METALLIC ADDITIVES

Any additive with a total metal content less than 0.1 percent was considered a non-metal. These ashless organic compounds were probably of the following types: amines, nitrates, oxygen-containing, nitrogen and/or sulfur in combination with oxygen, and halogen containing. The active ingredients in most non-metallic additives are apparently dissolved or suspended in mineral oil, light fuel oil, or other bases compatible with fuel oils. None of the non-metallic additives reduced total particulate emissions significantly at economically practical concentrations. Even at impractically high concentrations, only moderate reductions were noted.

## BURNER MODIFICATIONS

During the time the fuel additive testing was being conducted, Howekamp<sup>9,10</sup> also tested several burner modifications and demonstrated that three flame retention devices substantially reduced particulate emissions. Martin<sup>11</sup> subsequently compared the most effective burner modifications with the most effective additives. Burner modification appears to offer more promise for particulate reduction. In addition one of these devices also reduced  $\text{NO}_x$  emissions significantly; no additive tested showed any promise in this area. Figure 6

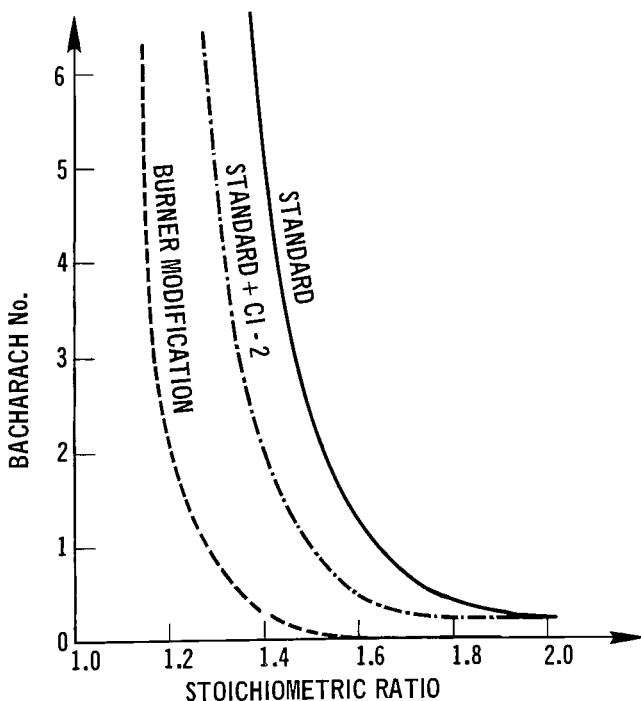


Figure 6. Comparison of effects of additives and burner modifications on particulate emissions.

permits comparison of the effects of additives and burner modifications on particulate emissions. At a given excess air setting, carbon particulate matter emitted by the modified burner with pure fuel is considerably less than that emitted by the standard burner or the standard burner with CI-2 in the fuel. These flame retention burners retail for about the same as a standard burner (\$70); a modification kit for use on existing burners is available for \$25. It should be noted that the optimum burner design for reduction of particulate matter and NO<sub>x</sub> emissions has not yet been achieved.



## CONCLUSIONS

1. In distillate oil no additive reduced  $\text{NO}_x$  or  $\text{SO}_x$  emissions, and only 17 out of 206 reduced particulate emissions. None of the 206 additives reduced unburned hydrocarbons or carbon monoxide.

2. Only proprietary metallic additives containing cobalt, iron, or manganese appreciably reduced particulate emissions. There is no evidence that a combination of metals in an additive offers any advantage over a single metal in an additive. Although a few non-metallic compounds seemed to reduce particulate emissions moderately, the concentrations required were too large to make them practical.

3. The most effective weight concentration for particulate reduction is highly dependent upon the specific additive; however, it appears that 0.5 millimole of total metal per kilogram of fuel is the optimum molar concentration and will be investigated further.

4. Arapahoe's Ferrocene and Ethyl's CI-2 reduced particulate emissions the most at practical concentrations. Further, Ferrocene, CI-2, and Fuelco  $\text{SO}_3$  (from Fuel Combustion Corporation) are the most economical of the effective additives. From a cost-effectiveness viewpoint Ferrocene and CI-2 are the most promising; however, the unknown toxicity of the metallic emissions they produce makes their use questionable. Moreover, commercially available flame retention devices can reduce particulate emissions more than any additive tested.

## **RECOMMENDATIONS**

1. Fuel additives should not be used as a means of controlling air pollutant emissions from distillate oil burning unless the metallic emissions they produce can be shown to be completely harmless.
2. Corrosion, fuel and additive stability, and long-term effects in addition to toxicity are areas of additive research that need detailed investigation before any general use could be recommended.
3. Fundamental research should be conducted to determine the mechanisms through which the most effective additives function and thereby gain an insight into the nature of the “optimum” fuel additive in terms of current knowledge.

## APPENDIX A.

### ADDITIVE LISTING

The information contained in this appendix was compiled from manufacturers' promotional material. Listing in this section does not constitute an endorsement by the Air Pollution Control Office. An effort was made to make this listing reasonably comprehensive, but a few manufacturers and specific additives may have been overlooked.

The test numbers shown in the second column correspond with the number found in column 1 of Appendix D. Note that some additives listed were not tested because of unavailability of samples. Note also that all dose figures are volume per volume unless indicated otherwise.

#### KEY TO SYMBOLS IN ADDITIVE LIST

AF	Antifouling	D	Dispersant
AH	Antihaze	DE	Demulsifying Agent
AN	Acid Neutralizing	E	Emulsifier
AO	Anti-Oxidant	GI	Gum Inhibitor
CA	Chelating Agent	OI	Oxidation Inhibitor
CC	Combustion Catalyst	PPD	Pour Point Depressant
CI	Combustion Improver	RI	Rust Inhibitor
CrI	Corrosion Inhibitor	S	Stabilizer
CS	Color Stabilizer	SAA	Surface Active Agent

## FUEL ADDITIVES

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
Acheson Colloids	1	Oil Dag	2-6	0.1 to 1.0 %	CI	Colloidal graphite-in-oil dispersion 10 % solids
	2	Oil Dag 170	2-6	0.1 to 1.0 %	CI	Semi-colloidal graphite-in-oil dispersion 40 % solids
Aetna Chemical Corporation		Actene A	1-6	1:2000 - 1:4000	D, E, CrI CI	Nonacid, noncaustic
		Actene C	R			
		Actene D-60	R			
A + L Labs		Actenite		Apply to firebox	VA-S inhibitor	Oxygen releasing solid
				1:1000	D, E, CrI	
Alben Daniels Chemical Corp.	3	Inferno	Heavy No. 1 and 2	1:3000	CI	
		Econodyne	2-6	1:1000	D, S, CrI CI	
Alken-Murray		Micheldyne	2-6		D	
	4	Evenflo 910	Bunker C	1:4500 - 1:7000	D, S, OI, DE	SAA-organic nitrogen
	5	Evenflo 910E	Bunker C	1:4500 - 1:7000	D, S, OI, DE	SAA-organic nitrogen
Alox Corporation	6	Evenflo HFS	Bunker C	1:6000 - 1:10,000	E, D	SAA-organic nitrogen
	7	Alox 488	Gasoline and diesel	6 oz of 20% add. in oil per 10 gal of gas	Lubricity	Ashless mixture of organic acids, oxy-acids, lactones, esters, and other oxygenated hydrocarbons
	8	Alox 1643	Residual	1:2000 - 1:4000	D	
	9	Alox 1846	Light dist.-jet fuel	4-20 lb per 1000 bbl	CI	

American Sand-Baunum	10	Sabanol	No. 4, 5, and 6	1:4000	D, CI, GI Va and sulfur inhibitor	Aromatic organic, emul- sifying agent
			Diesel, No. 1 and 2	1:8000	D, CI, GI, Va and sulfur in- hibitor	Rust inhibitor and agent to lower soot combus- tion temp.
	11	SLD				
	Amyloid	Pyrocat-E	Bunker C High S-Va	1:10,000	CI, slag inhibitor	Metal chelates
		Pyrocat-F	No. 6 and Bunker C	1:8000 - 1:10,000	CI, slag inhibitor	
		Pyrocat-NA	Residual- High NA	1:8000 - 1:10,000	CI, slag inhibitor	Metal chelates plus sodium complexing agent
		Pyrocat-SS	Heavy oils	1:10,000	S, CI	Organic
		Pyrocat-I	Heavy oils	1:5000	S, CI	Metal chelates
		Pyrocat-HV	Heavy oils		SO <sub>3</sub> reduction	Slurry—basic metal oxide
		Rolfite 404N	2-6	1:4000	Va-2 inhibitor SO <sub>3</sub> inhibitor	
	Andrew Rolfe Chemical Company	Rolfite 101N	Heavy oils, light oils in gas turbines	1:25,000	Va-S inhibitor SO <sub>3</sub> inhibitor CI, D	
		No-Smogg	Gasoline and Diesel	1:650 1:1000	CI, CrI	
		Rolfite Special			CI	

<sup>a</sup>As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

## FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
An-Pol	13	AnPol D	D	1:2000	S, E, D, CI	
	14	AnPol G	G	1:1000	E, D, CI	
	15	AnPol B	1-2		D	
	16	AnPol R	Residual		D, S, CI	
Apollo	17	DSD - 2	Distillate	1:4000 - 1:6000	D, CI, GI	
	18	SDI - 40	Distillate	1:2000	S, OI	
	19	MC - 7	Residual	1 gal per 600 - 800 bbl	Va and sulfur inhibitor, CI	Multipurpose catalyst
	20	SSI - 3	Hi-S residual	1:4000	CrI, CI, D SO <sub>x</sub> inhibitor	Multipurpose catalyst
	21	CC-2	Diesel	1:1000	D, CI, CrI	
	22	VCI - 4	Hi- Va and Na residual	1:4000	Va and sulfur inhibitor, D CI, GI	Metallic compounds
Arapahoe	23	Ferrocene		10 - 25 ppm	CI	Dicyclopentadienyl iron
Arol	24	Allite FS-12	No. 6	1:4000		
	25	Sludge Solvent	No. 6			
	26	Allite FOT	No. 6			
	27	P-D-5 Comb. Cat.	No. 6			
Baroid (National Lead)	28	Coat 907	Jet, diesel, No. 1, gas		CrI	Polar organic salts
Basic Chemical Company	29	Liquimag Mark VII	Bunker C	App. 0.1 - 0.5 wt %	CrI, Va and S inhibitor, SO <sub>3</sub> reduction	Magnesium oxides and other metallic oxides in oil 68% mass MgO, 8. 6 lb/gal, balance SiO <sub>2</sub> , CaO.

Bell Labs	30	Atom IX	No. 4, 5, and 6	1:2500	D, E, GI, CI	
	31	DEE - ZOL	Diesel		D, CI	
Berrymand	32	B - 12 Chem-tool	Diesel	1:25 - 1:50	E, D, CI	
Brilco Labs	33	Sludge Solvent		1:4000	D, E, S	Non-petroleum, all organic
Bryton	34	Hybase	Distillate	0.01 - 0.05% (vol)	D	14.5% (wt) Ba, 2% (wt) S, barium sulfonate
	35	Hybase C-300	Diesel Crankcase	15 - 20% (vol) 1 - 5% (vol)	CrI	11.6% (wt) Ca, 2% (wt) S, calcium sulfonate
	36	Hybase M-400	Diesel Crankcase	15 - 20% (vol) 1 - 5% (vol)	CrI	7.2% Mg, 2.0% (wt) S, magnesium sulfonate
Butler Engineering Association	37	Sul-Van-Kontrol				
	38	SK-3				
	39	TK-5				
Bystroms	40	Bycosin	G, D, 1-6	1:1000 - 1:2500	SAA, D	1.22% ash (99% iron oxide)
Cabot		Alon			Slag inhibitor	Fumed alumina
ATAKA and Co LTD (KAMEI Carbogen Ltd)	41	Blue Sky (Carbogen)	G	1:1500 - 1:3000	CI	Camphor oil, SAA o-dichlorobenzene
Carbo-Solv Lubricate	42	Fuel Oil Saver	No. 1 through No. 6	1:2000	AN, D, CI CrI, E	Alkaline, 27% Cl <sub>2</sub>
	43	Diesel F. OS.	Diesel	1:2000	AN, CI, D, E	

<sup>a</sup>As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

## FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
Carter Chemical Company	44	Coal Treat	Coal			
	45	Diesel Treat	Diesel			
	46	Fuel Treat "S"	Residual			
	47	Fuel Treat "2"	Distillate			
Castroleum Catalin	48	Casta Lube D	Diesel	1:320	AO	Degummed castor oil 9% (wt) sulfur. Aromatic sulfur organic
	49	CAO-6	Petroleum	0.5% (wt)		
Celanese	50	Methylal	Diesel	0.25-- 2.0%	Deposit reduction	CH <sub>3</sub> - O - CH <sub>2</sub> - O - CH <sub>3</sub>
Chemical Specialties Columbia-Bedford	51	CH-22	Hi Va-S residual	1:2000	CrI, SO <sub>3</sub>	MgO/Al <sub>2</sub> O <sub>3</sub> = 10/1, CaO, SiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> <1.5% each
		Klenn				
Combustion Cat. Corp.	52	Glo-Klen	Residual		CI, SO <sub>3</sub> inhibitor	Clay (Si, Na, Al, P)
Commercial Chemicals	53	Improsoot	Residual	1:1000 - 1:8000	D, E, CrI CI	Organic solvents, emulsifiers, catalysts
	54	Formula LSD	All grades	1:4000 - 1:8000	D, CI	Organic solvents, catalysts
	55	Improsite	All grades		D, E, CrI S	Organic solvents, emulsifiers
	56	Dispersite	All grades	1:4000 - 1:8000	D, S	
	57	Dispersoot	Coal	2 lb/100 boiler hq	Soot remover	



Crowley Tar Products	58	Cyclo-Flo	No. 6	1:1000	D	Petroleum base Mg, Al, Zr compounds petroleum base-40% active
	59	Vanadaban	No. 6	1 gal per 11 to 176 bbl	Va inhibitor	
Desmul	60	Heating Oil Catalysts		1:1000	CI	
	61	FE 4	Open flame burners	1:1280	CI	
	62	FE 6	Diesel and kerosene	1:1280	CI	
Dexson Chem. Co DiBattista	63	Gand		1:40 - 1:1000		
	64	(No Name)	No. 6	1:1000	E, SO <sub>2</sub> reduction	
Ditta Francesco Ferrerio R. Dona' Dryden Oil	65	Kryda	Fuel oils	1:1000 - 1:6000 mass basis	SO <sub>3</sub> inhib- itor, D, DE	All organic
	66	Sootrol	No. 6	10 gal per 1000 bbl	D	
DuPont	67	FOA - 2	Distillate and residual	5 - 60 lb per 1000 bbl	D, E	Copolymeric amine
	68	FOA - 3	Diesel and fuel oils	1 - 10 lb per 1000 gal	OA, AH, S	C, H, + N only (amine)
	69	D M D	Diesel and fuel oils	1/4 to 2 lb per 1000 bbl	Cooper de- activator	N, N' - disalicylidene 1, 2 - proponediamine
Eastman	70	Tenamene 60			Metal de- activator	N, N' - disalicylidene 1, 2 - proponediamine

<sup>a</sup>As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

## FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
Enjay	71	Paradyne 4	Distillate	0.002 - 0.01% (wt)	S	Ashless
	72	Paradyne 5		0.002-0.01% (wt)	S, DE	Ashless
	73	Paradyne 6	Distillate and residual	10 - 50 lb per 1000 bbl	DE, D	Ashless polymer
Erlen	74	No. 150 FOA	No. 1 - No. 6	1:4000 - 1:6000 (vol.)	SAA, D, CrI	
Ethyl	75	DB - 36	Diesel	1% (vol)	Cetane improver	Amyl nitrate
	76	DII - 2	Diesel	1% (vol)	Cetane improver	Hexyl nitrate
	77	MPA-D	Diesel	200 - 400 ppm	GI, D, detergent	Surface active organic
	78	CI - 2	No. 2 distillate	1 g Mn per gal	CI	24.7 wt% Mn, C <sub>9</sub> H <sub>7</sub> O <sub>3</sub> Mn
	79	Fuel Activator	G	1:1280	E, D, CI	
Fuel Activator Chemical Corp.	80	Diesel F.A.	D	1:3000	D, CI	
Fuel combustion Corp.	81	FUELCO	6		E, AN, D	
	82	FUELCO SO <sub>3</sub>	6	1:2000	CrI, DI	
		VASCONOL 3	H, Va - S residual	1:1000 - 1:3000	CrI, CI, SO <sub>3</sub> inhibitor	
	83	VASCONOL 4	H, Va - S residual	1:1000 - 1:3000	CrI, CI, SO <sub>3</sub> inhibitor	Mg pet. sulfonate
Garnlen Chemical Company	84	DP 231	D, 1 - 6		CI, CrI, Va - S-SO <sub>3</sub> inhibitor	Cresol and pet. derivatives, no halides

	85	Gamlenol Regular	R	1:1000 - 1:400	D	Cresol and pet. derivatives
Gibraltar	86	Diesel F. A.	Diesel	1:320 - 1:400	D, CI	
W. R. Grace	87	Dearsol 25	Fuel oil	1:4000	E, GI	
	88	Dearsol 30	Industrial fuel oil		Va and S inhibitor, CI, DE	
	89	Dearsol 35	Residual	1:4000	Va and S inhibitor, CI	Combustion catalyst
Harco Chemical	90	FT - 1	Coal			
	91	Oil Stabilizer	Residual	1:8000	S, SAA, E	
	92	HCC	Residual	1:5000	CI, CrI, Va and S inhib.	
	93	STAB + HCC	Residual	1:5000	Both of above	
	94	Harcoite Z	<sup>6</sup>		CI	Contains zirconium
Harlou	95	Fuel Oil Add.	Residual		CI	
Hoko Chemical Company	96	BHA	Residual	50 ppm	S oxidation accelerator, CI	Organic Enzyme
Hy-Test 303 Corp.	97	Heat NRG Fortifier	No. 2	1:4000	CrI, D, E,	
Industrial Chemical Company	98	INDUCO Supreme	G	1:480	D, E, CI	
	99	INDUCO Elite				
	100	INDUCO Diesel	D			
	101	INDUCO Delux				
	102	INDUCO BX 400	R	1:480	CI, D	
Industrial Chemicals,	103	Watcon 130	Fuel oils	1:1000	D	
	104	Watcon 140	Coal, oil	1 lb per 400 -	CI	Chlorides, sulphates,

<sup>a</sup>As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

## FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
Incorporated				600 gal		carbonates, and stearates of Zn, Na, and Cu. Cellulose and lignin
Lone Star	105	Texon	Diesel	1:480	D, S, DE CrI, CS	
Lubal Mfg. and	106	Combusto			D, DI, CrI	
Dist. Company	107	Lubal D	Diesel	1:1000	Detergent	
	108	Lubal Super D	Diesel	1:4000	CrI, detergent	
Lubrication Engineering	109	DCI	Diesel	1:150	CrI, CI, D, CS	
Lubrizol	110	520	No. 4, 5 and 6	7 - 10 gal per 1000 bbl	D, S, CI	
	111	560	Middle distillate	15 - 30 lb per 1000 bbl	DE, CrI, CI S, CS, D	
	112	585			D	
	113	565	Diesel	1:400 - 1:2000	CI	
Marine	114	Red Devel	Kerosene to	1:1250	D, E, CrI, CI	
Electrolysis		Soot Remover	Bunker C			
Eliminator						
Metropolitan	115	456	No. 4, 5, 6 and heavy	1:3000	D, E, S, CI	Alkaline
Petroleum and	116	456 SV	No. 4, 5, 6 and heavy	1:3000	Va and S inhibitor	Alkaline, organometallic soap
Petrochemical Corp.	117	Metlite	No. 2	1:3000	CI, DE, D	Alkaline, organometallic
	118	Metlite 2D+	Diesel	1:1500	CI, GI	Metal Organic
	119	Metspray	Coal			

N. A. Mogul	120	Fuel Oil Treatment	All fuel oils	1:1000	D	
	121	DP-2	Cat-cracked fuel oils	1:1000	S, D	
Monsanto	122	Santolene K	Diesel and fuel oils	20 - 30 lb per 1000 bbl	D, CrI	Non-metallic; mildly toxic
Nalco	123	151	Coal	1 lb per 3 - 6 tons	CI	Combustion catalyst
	124	152	Coal	1 lb per 3 - 6 tons	Slag removal	
	125	155	Residuals	1:1000 - 1:4000	AF, D, CI CrI	Combustion catalyst
	126	156-C	Coal	1 lb per 3 - 6 tons		
	127	158	Residuals	1:2000 - 1:4000	D, CrI, AF	Organic liquid, phenolic odor
	128	158-D	Residuals	1:2700 - 1:8000	D, S, CrI	Organic, aromatic odor, alkaline
	129	159	Diesel and Residuals	1:1000 - 1:8000	CrI	Organo-metallic blend in sulfur free hydrocarbon
	130	160-M	Distillate	2 - 15 lb per 1000 bbl	CrI	Organic liquid
	131	160-T	Distillate	5 - 40 ppm	CrI	Organic
	132	161	Petroleum process equipment	5 - 20 ppm	D, CrI	HMW polar organic liquid, no metals
	133	165-AC	Petroleum process equipment	2 - 5 ppm	CrI	Hydrocarbon
Nalco (cont'd)	134	262	Petroleum process equipment	>10 ppm (20 avg)	AF	N=3%, no halogens, HMW polar organic (ashless)

<sup>a</sup>As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

## FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
	135	303-AC	Distillate	5 lb per 1000 bbl minimum	S, D, CrI AO	Polymeric aliphatic amine, formaldehyde
	136	305	Jet and rocket fuel	5 - 30 lb per 1000 bbl (17 - 100 ppm)		
	137	D-1887	Furnace oils	1:8000	E, D, detergent, CrI, CC	
	138	D-1955	Distillate	2 lb per 1000 bbl	CS	As 303 AC
	139	D-1976	Distillate	2 lb per 1000 bbl	CS, D	As 303 AC and amine dispersant
	140	D-1991	Distillate	2 lb per 1000 bbl	C, S, D	As 303 AC and amine dispersant
	141	D-2015	Distillate	1 lb per 1000 bbl	D	Aromatic solvent and amine dispersant
New Surpass	142	Surpanate 960	Motor oil		D, CrI	2.7 wt% Ca; calcium petroleum sulfonate
	143	Surpanate 960C	Motor Oil		D, CrI, SO <sub>2</sub> - SO <sub>3</sub> neutralizer	Calcium petroleum sulfonate; colloidal Ca CO <sub>3</sub> (total Ca 11.5%)
Nitro Nobel AB		IPN	D	1:200	Cetane improver	Contains isopropyl nitrate
R. S. Norris and Associates	144	Barsad FOA-2	Diesel and residual	1:3000	D, CI	Contains calcium
	145	Barsad MN	No. 6	1 gal per 300 bbl	SO <sub>3</sub> inhibitor	Contains Mn
	146	Barsad S	No. 6		SO <sub>3</sub> inhibitor	Contains Mg

Norsemen	147	SP	Cord wood oil, and gas	100 g per ton fuel  1/2 lb per 5000 gal oil	Soot destruction   Applied to fire box
Olin Oxi-Kor Corporation Parke-Hill	148	Hydrazine Kor	No. 1 - No. 6	1:4000	D, CI
	149	Blue Heat	Distillate		CrI, CI, D, E
	150	Sludge Ban	Residual	1:1000	E, CrI, D
	151	Triple-X-100	Residual	1:1000	D, CrI
	152	Van Sul Ban	Residual	Hi S 3:10,000 Hi V 1:2000	D, CrI S and Va inhibitor CI
Perolin	153	Parko D-5	Diesel		CrI, Va - Na - S inhibitor
	154	PFOT 617-GM	Gas turbine residual		CrI, slag inhibitor; Va, Na inhibitor
	155	PFOT 626-DA	Residual	1:3000 - 1:4000	D, CrI, E, CI, Va-S inhibitor
	156	PFOT 644-EM	Residual	1:4000	CI, CrI, D, S
	157	PFOT 646-SP	Residual and distillate	1:2500 - 1:4000	CI
	158	PFOT 687-SD	Diesel	1:2500	CI, D, CrI
	159	Petrosene A	No. 2 and 4 No. 6	1:8000 1:4000	D, CrI
	160	Petrosene C	Distillate and	1:4000	SO <sub>3</sub> inhibitor
	161	Petrosene PM	Residual	1:2000	

<sup>a</sup>As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

## FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
Poly Phase	162	RX-613	Coal	1 lb per 10 tons		
	163	Anticor AC6-2	Coal and fuel oil	1 lb per 10 tons	CrI, Va and SO <sub>3</sub> inhibitor	
	164	Polyblend	Fuel oil	1:2000	D, E, CI	
	165	Polymag				
	166	Polyphase F106		1:1250		
Power Dynamics	167	Powerdyne 10	Fuel oil		CI, D	Each additive contains one of the following: organo metallics, metal slurries, amine types
	168	Powerdyne 12	Light oil		CI, D	
	169	Powerdyne 32	Heavy oil		Sa-Va inhibitor	
	170	Powerdyne 77	Light oil		D, DET, CI CrI	
Power Dynamics (cont'd)	171	Powerdyne 102	Coal		CI	
	172	Powerdyne 105	Coal		CI	
	173	Powerdyne 505	Heavy oil		S-Va inhibitor	
Rohm and Haas	174	Acryloid 917	Motor oil		D, PPD	Methacrylate ester
	175	Primene 81-R	Heating oil	10 to 30 lb per 1000 bbl	AO, S	Organic amine
H. E. Sanson	176	SYN-SOLV.	All fuel oil	1:5000 - 1:16000	D	Solvent
	177	T-H-R-U-S-T	Fuel oil	1:8000	E, CrI	
Sir Michael Thomas Chemicals Ltd.	178	S112 Concentrate	Heavy oils	1:3000	SO <sub>x</sub> inhibitor	
Solval Engineering	179	Pride	No. 4 and 6		Soot reduction, D	
		DC 25	2 - 4	Spot cleaner	D	
		APC 30	2 - 4	1:1000 - 1:4000	Soot reduction, D	



Studebaker Corp.	180	STP-Diesel Blitz	No. 1 diesel	1:800	D, CI detergent	100% petroleum; no sulfur
United Lubricants Ltd.		Isotane	Diesel		Smoker inhibitor	Isoprophyl nitrate
United (Oil Tech. Corp.)	181	Technol	No. 6	1:1000	CI, D, DET	
			No. 4	1:2000	PPD	
United (Oil Tech. Corp.) (cont'd)	182	Technol D	Diesel	1:300 - 1:400	CI, DET	Petroleum products, and hydrocarbons, no salts or metals
UOP	183	Technol G	Gasoline	1:300 - 1:350	CI, DET	
		Polyflo 100	No. 2	0.0005 - 0.005 wt%	D, S, PPD, D	Ashless polymeric amine
	184	Polyflo 120	1 - 2	14 - 56 g per m <sup>3</sup>	CS, DE, PPD	As 100 plus demulsifier
	185	Polyflo 121	Distillate	14 - 28 g per m <sup>3</sup>	CS, DE, PPD	Poloyflo 120 w copper deactivator added
	186	Polyflo 122	Diesel and distillate	0.0005 - 0.10 wt%	CA	Similar to above
	187	Polyflo 130	Distillate	0.0005 - 0.005 wt%	OI, CS, AF	
	188	Polyflo 135	Crude	10 - 40 ppm	CI, AH	Replace Polyflo 100
					CI, D, S, PPD	
					AF, OI	Polymeric amine and antioxidant
	189	Polyflo 140	Distillate	10 - 1000 ppm	AF, S, PPD	Improved 100 and 130
R. T. Vanderbilt Company, Incorporated.	190	Vanlube PC	Distillate		OI	Substituted phenol
	191	Vanlube 601	Pet. fuels	0.02 - 0.2%	CA, CI	Heterocyclic nitrogen-sulfur

<sup>a</sup> As taken from manufacturers' literature. No attempt at verification was made by the Air Pollution Control Office.

# FUEL ADDITIVES (Continued)

Manufacturer	Test No.	Additive	Type fuel	Dose <sup>a</sup>	Function <sup>a</sup>	Description <sup>a</sup>
	192	NA-SUL AS	Pet. fuels		RI	Chain-ring organic with SO <sub>3</sub> NH <sub>4</sub> ; 50% in mineral oil
R. T. Vanderbilt Company Incorporated (cont'd)	193	NA-SUL EDS	Pet. fuels		RI, CI	Chain-ring organic, diamine and SO <sub>3</sub> , 50% in kerosene
	194	NA-SUL LP	Distillate		CI	Chain-ring organic, diamine and SO <sub>3</sub> , 50% in kerosene
	195	Cuvan 80	Distillate	0.5 - 12 lb per 1000 bbl	CA, S	Cycle diamine, 80% in org. sol
W-6, Inc. Witco	196	W - 6	D, 1 - 6	1:4000	D, CrI, CI	
	197	300 Base Calcium petronate				3% Ca; Ca sulfonate 45%; 0.25% Cl <sub>2</sub> ; 0.1% Na
Whitnor	198	W - 2	Gasoline and diesel Fuel Oil	0.025 - 01 wt%  1 gal (50% w-2 and 50% Naphenic oil) per 4000 gal	D, CrI	
Wonder-King Chemical Company Wynn	199	Methyl High-Test			G, D, DI	
	200	Sludge Klean	No. 2, 4, 5 and 6		D	
	201	Bunker fuel add	Bunker	1:1000-1:4000	D, S, CI, AN	

Wynn (cont'd)	202	Furnace Fuel Conditioner	Distillate	1:000 - 1:2000	D, DE, CrI, Cl, SO <sub>x</sub> reduction	
Zep	203	Formula 221	Fuel oil	1:400 - 1:10,000	D, E, CrI	Hydrocarbon fraction, SAA ethane oxide, monoethanol amine
W. E. Zimmie, Inc.	204	Comb. Cat 405	Oil Coal	1:500 - 1:7000	Cl, CC, SO <sub>3</sub> inhibitor	
	205	Fuel Oil Stabi- lizer ZF 400	Residual	1:4000	Cl, CrI, D, E	
	206	Zimmite 455		1:4000		Combined 400 and 405

## APPENDIX B.

### LIST OF ADDITIVE MANUFACTURERS

<u>Company</u>	<u>Address</u>	<u>Phone</u>
Acheson Colloids	Port Huron, Mich.	----
Aetna Chemical Corp.	Wallace St. Extension East Patterson, N. J.	796-0230
Alben Daniels Chemical Corp.	P.O. Box 148 Hyattsville, Md.	----
Alken-Murray Corp.	111 Fifth Avenue New York, N.Y. 10003	777-6560
Alox Corp.	P.O. Box 517 Niagara Falls, N.Y. 14302	282-1295
American San Banum Company	1 Merrick Avenue Merick, N.Y. 11566	378-3390
Amoco Petrofina SA	33 Rue De La Loi Bruxelles 4, Belgium	12.01.60.10 Lignes
Amyloid, Inc.	322 Main Street Stamford, Conn. 06901	324-9788
Andrew Rolfe Chemical Company	900 Bedford Street Stamford, Conn. 06902	327-3151
An Pol	P.O. Box 20259 Long Beach, Calif. 90801	436-1297
Apollo Chemical Corp.	250 Delawanna Avenue Clifton, N.J. 07014	472-5400
Arapahoe Chemicals	2855 Walnut Street Boulder, Colo. 80302	442-1926
Arol Chemical Products Company	371-81 Wayne Street Jersey City, N.J. 07302	432-4710

<u>Company</u>	<u>Address</u>	<u>Phone</u>
Baroid Division National Lead Company	P.O. Box 1675 Houston, Texas 77001	524-6381
Basic Chemicals	845 Hanna Building Cleveland, Ohio 44115	241-5000
Bell Laboratory	2421 Kilgore Avenue Orlando, Fla. 32803	422-2568
Berryman Products, Inc.	P.O. Box 1016 San Jose, Calif. 95108	----
Brilco Laboratories	1553 63rd Street Brooklyn, N.Y. 11219	236-3812
Bryton Chemical Company	9 Rockefeller Plaza New York, N.Y. 10020	586-2510
Butler Engineering Assoc.	764 Ramsey Avenue Hillside, N.J. 07205	688-3300
Carbo-Solv Lubricite Corp.	4144 Sheridan Road Chicago, Ill. 60613	935-4548
Carter Chemical Company		
Castroleum	31 Fullerton Avenue Yonkers, N.Y. 10704	476-7210
Catalin Corp.	1 Park Avenue New York, N.Y. 10016	683-2100
Celanese Chemical Company	245 Park Avenue New York, N.Y. 10017	867-2000
Chemical Specialities Corp.	75 Hillside Road Fairfield, Conn. 06430	255-2804
Columbia-Bedford Corp.	44 Whitehall Street New York, N.Y. 10025	269-1457
Combustion Catalyst Corp.	1731 Munsey Building Baltimore, Md. 21202	685-2484

<u>Company</u>	<u>Address</u>	<u>Phone</u>
Crowley Tar Products	271 Madison Avenue New York, N.Y. 10016	683-1040
Desmul Chemical Company	Pier 66 Seattle, Wash. 98121	623-6356
Dexson Chemical Corp.	407 Weatherly Building Portland, Ore. 97214	233-6422
DiBattista, Charles	716 Willow Street Cranford, N.J.	
Ditta Francesco Ferrerio R Dona	10-12 Via Donatello Milano, Italy	200.281
Dryden Oil Company	Braddish Avenue and WMRR Baltimore, Md. 21216	233-2000
DuPont Petroleum Lab.	Wilmington, Del. 19898	299-5000
Eastman Chemical Products	Chemicals Division Kingsport, Tenn. 37662	246-2111
Enjay Chemical Company	60 West 49th Street New York, N.Y. 10020	
Erlen Products	700 South Flower Street Burbank, Calif. 91502	849-6591
Ethyl Corp.	100 Park Avenue New York, N.Y. 10017	679-2000
Fuel Activator Chemical Corp.		
Fuel Combustion Corp.	745 Fifth Avenue New York, N.Y. 10002	753-0078
Gamlen Chemical Company	11 Broadway New York, N.Y. 1000	
Gibraltar Refining and Chemical Company	Manor, Penn. 15665	863-3400
W. R. Grace and Company	Merchandise Mart. Plaza Chicago, Ill. 60654	527-3273

<u>Company</u>	<u>Address</u>	<u>Phone</u>
Harco Chemical Company	338 North Avenue E. Cranford, N.J. 07016	276-1096
Harlou Products Corp.	23-37 51st Avenue Long Island City 1, N.Y.	784-9340
Hoko Chemical Company	341 Daigiri, Fujisawa-shi, Kanagawa Prefecture, Japan	
Hy-test 303 Corp.	9 Meadow Road Rutherford, N.J. 07105	933-0300
Industrial Chemical Company	P.O. Box 78 Cupertino, Calif. 95014	
Industrial Chemicals, Inc.	2215 South Main Street South Bend, Ind. 46613	287-3397
Lone Star Chemical Company	P.O. Box 26777 Houston, Texas 77032	643-9406
Lubal Mfg. and Dist. Company	375 West Rich Street Columbus, Ohio 43223	221-4674
Lubrication Engineers	3851 Riverside Freeway Fort Worth, Texas 76111	834-6321
Lubizol Corp.	29400 Lakeland Blvd. Cleveland, Ohio 44117	943-4200
Marine Electrolysis Eliminator	1137 SW Hanford Street Seattle, Washington 98134	624-2266
Metropolitan Petroleum Petrochemicals	235 East 42nd Street New York, N.Y. 10017	867-4141
North American Mogul Products Company	Standard Building Cleveland, Ohio 44113	
Monsanto Company	800 N. Lindbergh Blvd. St. Louis, Mo. 63166	694-1000
Nalco Chemical Company	180 North Michigan Avenue Chicago, Ill. 60601	

<u>Company</u>	<u>Address</u>	<u>Phone</u>
New Surpass Petrochemical Ltd.	36 Upton Road Scarborough, Ontario, Can.	751-6100
Nitro Nobel A. B.	Stockholm, Sweden	
R.S. Norris and Assoc.	26 Valley Road Larchmont, N.Y. 10538	834-4195
Norsemen Chemical Ltd.	P.O. Box 16 Rungsted Kyst, Denmark	864121
Oil Technology Corp.	99 E. Hawthorne Avenue Valley Stream, N.Y. 11580	593-3711
Olin Chemicals	460 Park Avenue New York, N.Y. 10022	572-3000
Oxi-Kor Corp.	600 West 9th Avenue Gary, Indiana 46401	883-8567
Parke Hill Chemical Corp.	29 Bertel Avenue Mont Vernon, N.Y. 10550	688-7220
Perolin Company	350 Fifth Avenue New York, N.Y. 10001	947-8987
Poly Phase Chemical Service	180 Hempstead Turnpike W. Hempstead, L.I., N.Y. 11552	485-6161
Power Dynamics Corp.	P.O. Box 145 Boston, Mass. 02101	542-7634
Rohm and Hass Company	Independence Mall West Philadelphia, Penn.	592-3000
H. E. Sanson and Sons, Inc.	2215-25 North American St. Philadelphia, Penn. 19133	426-7723
Sir Michael Thomas, Ltd.	Musk Lane, Lower Gornal, Dudley Worchestershire, England	3852454
Solval Engineering Corp.	Massey Hill Road E. Swanzey, N.H. 03446	352-4879



<u>Company</u>	<u>Address</u>	<u>Phone</u>
Studebaker Corp.	635 South Main Street South Bend, Inc. 46618	
United Lubricants, Ltd.	Address Unknown Assumed Defunct.	
UOP Process Division	30 Algonquin Road Des Plains, Ill. 60016	763-6000
R. T. Vanderbilt Company	230 Park Avenue New York, N.Y. 10017	686-6864
W - 6, Inc.	P.O. Box 3146 Inglewood, Calif. 90304	677-5345
Witco Chemical Company	75 E. Wacker Drive Chicago, Ill.	346-2960
Whitnor Chemicals	Model City, N.Y. 14107	754-4008
Wonder King Chemical Corp.	31 New Haven Railroad Street Mount Vernon, N.Y.	688-4078
Wynn Oil Company	1151 West 5th Street Azusa, Calif. 91703	334-0231
Zep Manufacturing Company	1310 Seaboard Industrial Blvd. NW Atlanta, Ga. 30301	
W. E. Zimmie, Inc.	810 Sharon Drive Westlake, Ohio 44145	871-9660

## **APPENDIX C.**

### **ANALYTICAL PROCEDURES**

#### **PARTICULATE MATTER**

The particulate sampling train consisted of a Pryex glass probe (1-7/16-inch i.d.) with an integral filter. A fiber glass filter paper (MSA 1106BH) 2 inches in diameter was used with a sintered-glass back-up plate. The filter was followed by an air-cooled section of glass tubing, which was connected to a series of three glass water bubblers and one dry trap. The bubblers and trap were immersed in a water bath at 32° F. The trap was followed by a second fiber glass filter.

Gas flow rates were measured with a calibrated orifice and manometer; isokinetic sampling rates were maintained. A dry-gas meter was used to measure the total sample volume. Preliminary tests were made to locate a point in the sampling stack where average particulate concentrations could be obtained.

After sampling, material inside the probe was combined with the filtered solids. Filter temperatures were not controlled, but were somewhat below the flue gas temperatures. Condensation on the filter was not encountered.

The weight of the material collected in the bubblers and trap, referred to as condensables, was also determined in some cases.

Each particulate determination for air-fuel ratios of 1.50 and higher was an integrated sample accumulated over six cycles. Particulate emissions were so much greater at stoichiometric ratios of 1.0 and 1.10, that each 10-minute "burner on" period had to be divided into five 2-minute sampling periods. Thus, five separate, consecutive samples were required to cover the 10-minute "burner on" period.

#### **SMOKE**

Smoke levels were determined automatically with a sequential tape sampler incorporating a light transmission recorder. The instrument was modified to take samples equivalent to the smoke number measurements of the Shell-Bacharach index, which is widely used to evaluate the performance of oil burners. The flue gas sample was drawn through a water-cooled probe with a condensate trap. Each smoke spot was taken in 48 seconds (12 seconds being required to advance the tape between samples). Ten smoke measurements were made during each 10-minute "burner on" period.

The tapes were later scanned with a Shell-Bacharach index to give a visual light reflectance reading for comparison with the light transmission readings. A graph relating the smoke index to Cohs per 1000 feet from the light transmission meter is shown in Figure C-1. The upper limit of measurements for the Shell-Bacharach index<sup>1 2</sup> corresponds to a value of 425 Cohs per 1000 feet. Approximately 1200 Cohs per 1000 feet is the upper limit for the transmission instrument. At every smoke number reading there was an overlap with smoke density at the next higher and lower smoke numbers. For a given smoke density, a range of Bacharach smoke index is shown in Figure C-1 and is attributable to the variation in visual evaluation of the Bacharach smoke index.

## CARBON DIOXIDE, OXYGEN, CARBON MONOXIDE, AND GASEOUS HYDROCARBONS

Automatic instruments were used to continuously record the concentrations of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , and gaseous hydrocarbons in the flue gas.  $\text{CO}_2$  was measured by a nondispersive infrared analyzer;  $\text{O}_2$  was measured by a paramagnetic-type instrument;  $\text{CO}$  was measured by a nondispersive infrared analyzer; gaseous hydrocarbons were measured by a flame ionization analyzer. The instrument ranges available were 0 to 16 percent for  $\text{CO}_2$ ; 0 to 21 percent of  $\text{O}_2$ ; 0 to 500 ppm, 0 to 1500 ppm, and 0 to 2 percent for  $\text{CO}$ ; and 0 to 100 ppm and up for gaseous hydrocarbons (calibrated as propane).

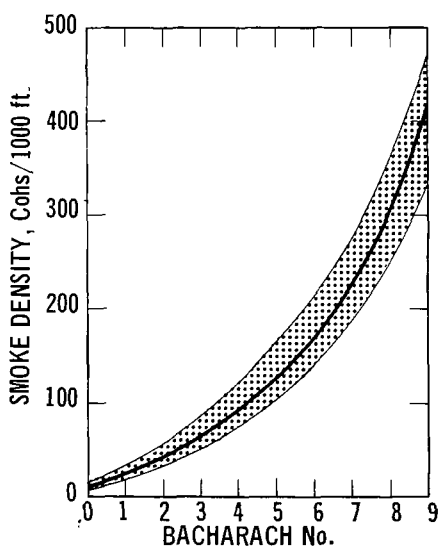


Figure C-1. Bacharach No. versus smoke density.

## OXIDES OF NITROGEN

Total nitrogen oxide concentrations were measured from 2-liter integrated samples taken over the 10-minute "burner on" period. Since sulfur dioxide was present in the sample gas, the phenoldisulfonic acid method<sup>13</sup> was chosen for the analysis. During the later stages of the work, this method was checked with long-path nondispersive infrared analysis and the agreement was quite satisfactory. Instrument ranges available were 0 to 150 ppm, 0 to 750 ppm, and 0 to 1500 ppm.

A stainless steel sampling prob (1/4-in. o.d. by 14 inches long) was used in the testing. The collection flask was a 2-liter round-bottom flask with an outer 24/40 joint for integrated samples. Figure C-2 shows the details of the orifice assembly. A flow rate of about 1 liter per minute was maintained. The spectrophotometer used in this work was a Beckman Model B.

The analytical testing required several different reagents, which are described below.

1. 30 percent Hydrogen Peroxide (reagent grade).
2. \*3 percent Hydrogen Peroxide. Dilute 30 percent  $\text{H}_2\text{O}_2$  with water at 1:10 ratio. Prepare fresh daily.
3. Concentrated Sulfuric Acid.
4. 0.1N (approximate) Sulfuric Acid. Dilute 2.8 ml concentrated  $\text{H}_2\text{SO}_4$  to 1 liter with water.
5. Absorbing Solution. Add 12 drops 3 percent  $\text{H}_2\text{O}_2$  to each 100 ml 0.1N  $\text{H}_2\text{SO}_4$ . Make enough for required number of tests.

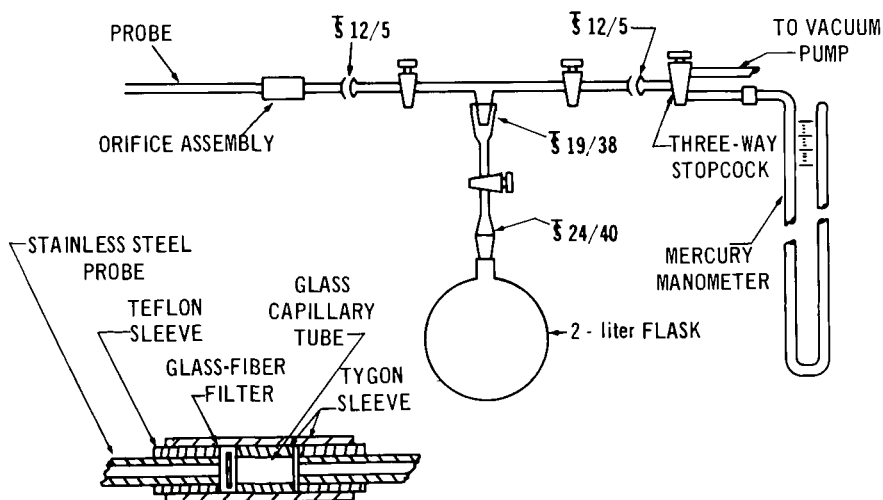


Figure C-2. Integrated sample apparatus with detail of critical orifice assembly.

6. 1N (approximate) Sodium Hydroxide. Dissolve 40 g NaOH pellets in water and dilute to 1 liter.
7. Concentrated Ammonium Hydroxide.
8. Fuming Sulfuric Acid. 15-18 weight percent free sulfuric anhydride (oleum).
9. Phenol (reagent grade).
10. Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol in 150 ml concentrated  $\text{H}_2\text{SO}_4$  on a steam bath. Cool and add 75 ml fuming sulfuric acid. Heat to  $100^\circ\text{C}$  for 2 hours. Store in a dark, stoppered bottle. This solution should be colorless if prepared from quality reagents.
11. Potassium Nitrate (reagent grade).
12. Standard Potassium Nitrate Solution. Solution A: Dissolve 0.5495 g  $\text{KNO}_3$  and dilute to 1 liter in a volumetric flask. Solution B: Dilute 100 ml of Solution A to 1 liter. One ml of Solution A contains the equivalent of 0.250 mg  $\text{NO}_2$  and of Solution B, 0.0250 mg  $\text{NO}_2$ .

Following a sampling period, the collection flask was shaken for 15 minutes and allowed to stand overnight. The contents were then transferred into a beaker, and the flask washed three times with 15-milliliter portions of  $\text{H}_2\text{O}$ . These washings were then added to the solution in the beaker. For a blank, 25 milliliters of absorbing solution and 15 milliliters of  $\text{H}_2\text{O}$  were added to a beaker. From this point on, both the blank beaker and the test beaker were processed according to the following scheme.

1 N NaOH was added to the beaker in question until the solution showed just alkaline on litmus paper. Next the solution was evaporated to dryness on a water bath, and 2 milliliters of phenoldisulfonic acid solution was carefully added to the dried residue. Four drops of concentrated  $\text{H}_2\text{SO}_4$  and 2 milliliters of  $\text{H}_2\text{O}$  were then added.

After the solution was allowed to cool, 25 milliliters of  $\text{H}_2\text{O}$ , 10 ml concentrated  $\text{NH}_4\text{OH}$  was added dropwise, and the solution allowed to cool again. All samples were filtered, diluted with water, and thoroughly mixed. Finally, the absorbency was read for each sample at 420 millimicrons. If the absorbency was higher than 0.60, a suitable dilution was made. The final calculations were made by using the following formula.

$$\text{ppm NO}_2 = \frac{(5.24 \times 10^5)(C)}{V_5}$$

where C = concentration of  $\text{NO}_2$ , mg from a calibration chart

$V_5$  = gas sample volume in ml at  $70^\circ\text{F}$  and 29.92 in Hg

## OXIDES OF SULFUR

Concentrations of sulfur dioxide and sulfur trioxide were measured from 25-liter integrated samples taken over a 10-minute "burner on" period. Sulfur

trioxide was collected by the Combustion Engineering condensation technique<sup>14</sup> in which the temperature is maintained below the dew point of  $\text{SO}_3$  and above that of water. Sulfur dioxide was collected in hydrogen peroxide solution in a bubbler. Analysis of the  $\text{SO}_3$  and  $\text{SO}_2$  was done by the Shell method.<sup>15</sup> Interference from particulate matter, which may contain metal sulfates, cations that complex with the indication as coprecipitate barium, or phosphates, was eliminated by means of a silica wool filter.

The sampling equipment used in this work is shown in Figure C-3. The reagents that were used in the analysis are listed below along with a description of how to prepare them.

1. Isopropyl alcohol, anhydrous.
2. 80% Isopropyl Alcohol. Dilute anhydrous isopropyl alcohol 4 to 1 with distilled water.
3. 3% Hydrogen Peroxide. Dilute 30% hydrogen peroxide 1 to 9 with distilled water.
4. Standard 0.00500 Formal Barium Perchlorate. Dissolve 1.9516 g barium perchlorate,  $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , in 200 ml distilled water and dilute to 1 liter with anhydrous isopropyl alcohol. Standardize this solution against standard 0.01N sulfuric acid containing 80% isopropyl alcohol in its final volume.
5. Standard 0.01N Sulfuric Acid (0.005 formal in sulfate ion). Pipet 100 ml purchased, prestandardized 0.1N  $\text{H}_2\text{SO}_4$  into a 1-liter volumetric flask and, add 100 ml distilled water. Make up to 1 liter with anhydrous isopropyl alcohol.
6. Thorin Indicator. 1-(0-arsonophenylazo) 2-naphthol-3,6-disulfonic acid, disodium salt. Dissolve 0.2 g thorin in 100 ml distilled water. Store in polyethylene container. Thorin solution deteriorates if stored in glass container.

The sampling procedures that were given to the technicians for use in this work are listed below for completeness. The analytical method is from Shell Development.

## SAMPLING PROCEDURE

Set up apparatus as shown in Figure C-3. Wrap the fritted disk up to the inlet of the bubbler with asbestos tape; any water condensation would be likely to contain some  $\text{SO}_2$  as sulfurous acid, which would, if oxidized, be mistaken as  $\text{SO}_3$ . Evacuate the tank(s) and check for leaks. Record manometer readings, temperature, and barometric pressure. Sample at a rate of 2 to 3 liters per minute. At end of test, again record manometer readings and temperature. Disassemble sampling train. Save the silica wool filter used at the tip of the

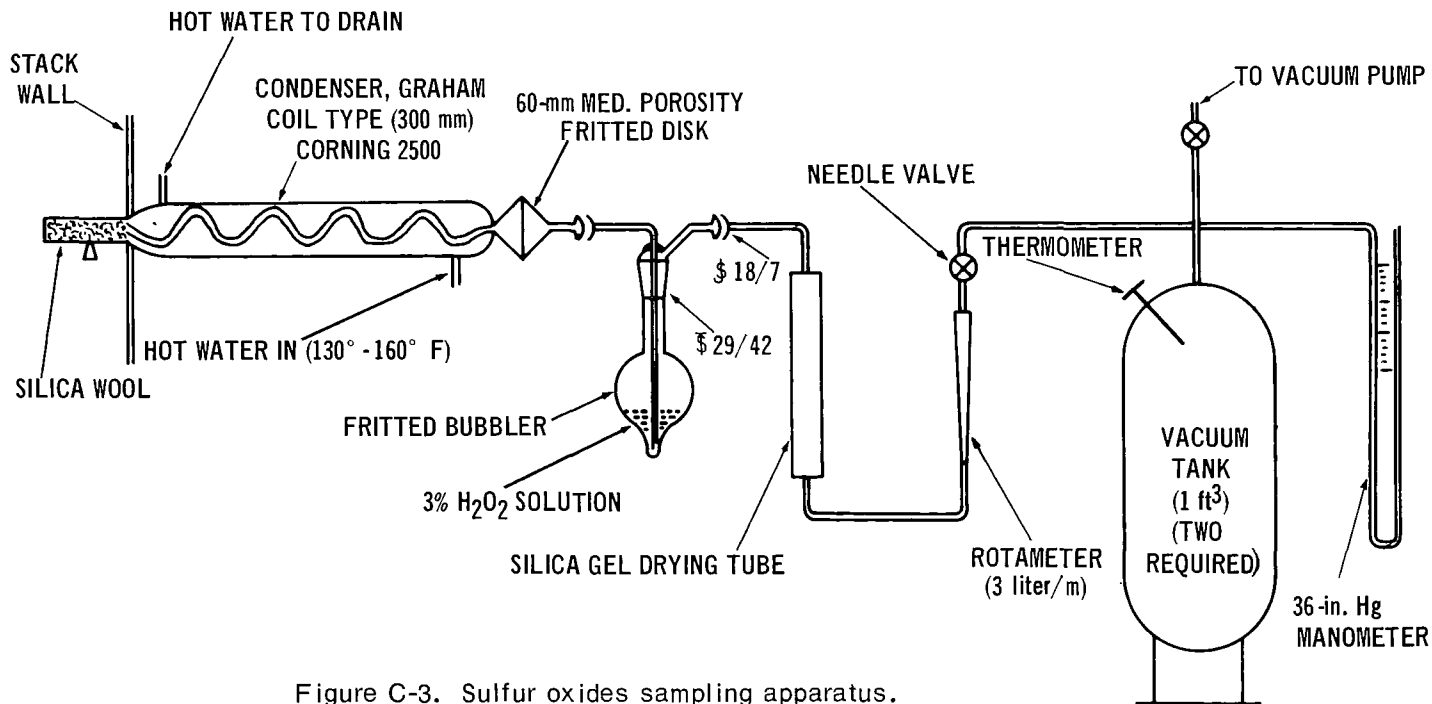


Figure C-3. Sulfur oxides sampling apparatus.

condenser for reuse. Flue gas conditioning of a fresh filter plug is desirable to prevent  $\text{SO}_3$  adsorption.

## ANALYSIS

### Sulfur Trioxide

Mount the condenser in a vertical position, as shown in Figure C-4, with a graduated Erlenmeyer flask as a receiver on the lower end. Apply a vacuum at this end, and rinse condenser with one 20-milliliter portion followed by two 10-milliliter portions of distilled water from a graduated cylinder. Add in a way that ensures that the entire fritted disk is contacted. To the 40 milliliters of rinsings in the flask, add 160 milliliters of anhydrous isopropyl alcohol (to obtain an 80 percent alcohol solution) and 2 or 3 drops of thorin indicator (enough to give a yellow color). Titrate with standard barium perchlorate to the pink endpoint. Run a blank determination in parallel.

### Sulfur Dioxide

Pour the bubbler contents into an Erlenmeyer flask and rinse the bubbler with distilled water to obtain approximately 40 milliliters of solution total. Add 4 times this amount of anhydrous isopropyl alcohol (160 ml) to obtain an 80 percent alcohol solution. Add 2 or 3 drops of thorin indicator, and titrate to the pink endpoint with standard barium perchlorate. Run a blank determination in parallel.

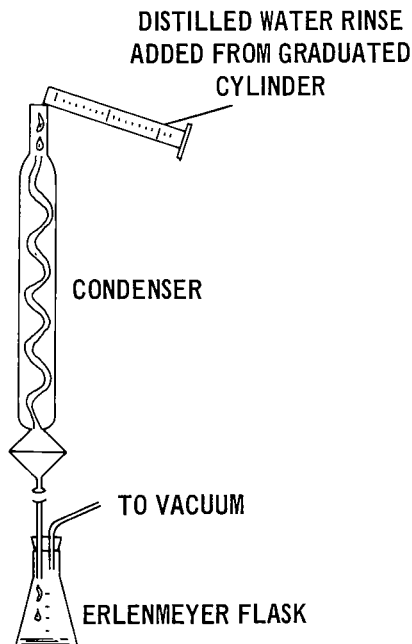


Figure C-4. Sulfur trioxide sampler.



## **APPENDIX D.**

### **EXPERIMENTAL RESULTS**

This section contains the actual experimental results of this program. Additives may be identified by referring to the corresponding number in Appendix A.

## TEST RESULTS AND ADDITIVE ANALYSIS

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%							
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals
1.	NT <sup>b</sup>					86.4	10.9	<0.1	0.3	ND <sup>c</sup>	2.4	<0.2	
2.	NT					87.7	12.1	<0.1	0.2	ND	nil	<0.2	
3.	1:370	1.0	1.0	1.0	1.0	81.3	11.7	<0.1	0.8	ND	6.2	<0.2	Na = 0.42
4.	1:4500	1.0	ND	1.0	1.0	85.8	10.8	0.2	<0.1	ND	3.2	<0.2	
5.	1:4500	1.0	ND	1.0	1.0	71.2	9.0	0.3	<0.1	0.1	19.4	<0.2	
6.	1:475	1.0	1.0	1.0	1.0	67.8	7.7	<0.1	0.3	<0.1	22.5	1.7	K = 0.34 Na = 0.34
	1:6000	1.0	1.0	1.0	1.0								
7.	NT					83.5	13.0	<0.1	<0.1	ND	3.5	<0.2	
8.	1:2000	1.35	ND	1.0	1.0	85.1	13.1	<0.1	<0.1	ND	1.8	<0.2	
9.	1:12,600	0.84	ND	1.0	1.0	78.7	12.7	0.7	0.3	ND	7.6	<0.2	
10.	NT					90.2	7.4	0.5	0.5	ND	0.6	0.8	Pb = 0.48
11.	1:2360	1.25	1.0	1.0	1.0	53.1	8.4	<0.1	0.9	ND	9.6	28.	Ba = 16.2

12.	1:1000	1.0	1.0	1.0	1.0	84.6	12.4	0.2	0.6	ND	1.8	0.4	Mn = 0.2	
	1:500	1.0	1.0	1.0	1.0									
13.	1:4000	1.0	1.0	1.0	1.0	83.5	12.4	0.6	<0.1	ND	3.3	0.2	Ba = 0.1	
	1:2000	1.0	ND	1.0	1.0									
	1:1000	1.0	ND	1.0	1.0									
	1:500	1.0	ND	1.0	1.0									
	1:250	1.0	1.0	1.0	1.0									
	1:125	1.0	1.0	1.0	1.0									
14.	1:2000	1.0	ND	1.0	1.0	83.7	12.1	0.5	<0.1	ND	3.7	<0.1		
	1:1500	1.0	ND	1.0	1.0									
	1:1000	1.0	ND	1.0	1.0									
	1:750	1.0	ND	1.0	1.0									
	1:500	1.0	ND	1.0	1.0									
	1:250	0.78	ND	1.0	1.0									
15.	1:1000	0.83	0.83	1.0	1.0	83.0	12.4	0.4	<0.1	ND	4.0	0.2	Ba = 0.1	
16.	1:1000	0.86	0.86			83.5	12.6	0.3	<0.1	ND	3.4	0.2	Ba = 0.1	
17.	1:860	1.0	0.74	1.0	1.0	71.4	10.2	0.6	0.2	ND	11.6	6.0	Pb = 0.9 Mn = 0.6 Ba = 0.6	Ca = 0.48 Sn = 0.30 Si = 0.18

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%							
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals
18.	1:11,200	1.0	ND <sup>c</sup>	1.0	1.0	67.0	10.4	0.7	1.6	ND	2.3	18.	Ba = 7.2    Pb = 0.05 Ca - 0.18
	1:5,600	1.0	ND	1.0	1.0								
	1:2,240	1.0	ND	1.0	1.0								
	1:1,120	1.0	0.89	1.0	1.0								
	1:560	1.68	ND	1.0	1.0								
19.	1:13,600	1.0	1.0	1.0	1.0	33.7	5.8	0.3	0.4	ND	7.8	52.	Mn = 24.8    Fe = 1.0 Ba = 6.9    Si = 2.4 Al = 1.3    Ca = 0.41
20.	1:9100	1.0	1.0	1.0	1.0	39.0	5.5	0.1	0.4	0.3	37.7	17.	Mg = 10.    Mn = 0.85 Ba = 0.85    Sb = 0.34
21.	1:920	1.0	0.89	1.0	1.0	80.1	11.7	0.1	0.4	ND	2.5	5.2	Zn - 3.0 Ba = 1.0
22.	1:21,500	1.0	1.0	1.0	1.0	39.8	7.7	<0.1	0.3	0.1	17.1	35.	Mg = 10.    Sb = 0.34 Mn = 0.85    Ca = 0.21
23.	1:28,600	1.0	1.0	1.0	1.0	65.6	5.8	<0.1	0.1	ND	1.5	27.0	Fe = 20.
	1:11,900	0.65	0.59	1.0	1.0								
	1:8,925	0.68	0.59	1.0	1.0								
	1:7,150	0.55	0.46	1.0	1.0								

	1:5,360	0.64	0.44	1.0	1.0												
	1:3,775	0.53	0.34	1.0	1.0												
24.	1:4000	1.15	ND	1.0	1.0	40.6	5.0	<0.1	0.1	24.3	30.1	<0.2					
25.	1:4000	1.0	ND	1.0	1.0	73.6	9.4	0.1	<0.1	1.4	15.6	<0.2					
26.	1:4000	1.0	ND	1.0	1.0	77.8	8.0	<0.1	<0.1	1.2	13.0	<0.2					
27.	1:4000	1.0	1.0	1.0	1.0	80.4	11.8	<0.1	<0.2	ND	5.8	2.0				Zr = 1.0	
																	Pb = 0.04
28.	1:4000	1.0	ND	1.0	1.0	81.5	13.8	0.2	<0.1	ND	4.5	<0.2					
29.	NT <sup>b</sup>					35.5	5.3	<0.1	<0.1	ND	5.2	54.				Mg = 35.	Al = 0.5
																Ca = 1.5	Fe = 0.25
																Se = 1.0	Pb = 0.15
30.	1:2500	1.0	ND	1.0	1.0	85.9	14.0	<0.1	0.1	ND	nil	<0.2					
31.	1:1000	1.0	ND	1.0	1.0	86.0	14.0	<0.1	0.1	ND	nil	<0.2					
	1:50	1.0	ND	1.0	1.0												
32.	1:1000	1.0	ND	1.0	1.0	74.3	10.9	<0.1	0.2	ND	14.6	<0.2					
	1:50	1.0	ND	1.0	1.0												

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%							
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals
33.	1:4000	1.0	ND <sup>c</sup>	1.0	1.0	89.8	7.6	0.7	0.7	ND	1.2	<0.2	
34.	1:1900	1.0	1.0	1.0	1.0	62.2	9.8	<0.1	3.1	ND	nil	25.	Ba = 13.0 Ca - 0.05
35.	1:6000	1.0	1.0	1.0	1.0	58.6	9.0	<0.1	1.7	ND	8.7	22.	Ca = 12
36.	1:4650	1.16	1.0	1.0	1.0	62.8	10.1	<0.1	1.9	ND	11.2	14.	Mg - 5.6
37.	1:440	1.27	1.24	1.0	1.0	86.5	12.2	0.1	<0.1	ND	0.3	0.9	Mg = 0.4    Pb = 0.07 P = 0.1      Co = 0.05
38.	1:400	1.0	ND	1.0	1.0	86.1	13.3	<0.1	<0.1	ND	0.6	<0.2	
39.	1:420	1.42	1.24	1.0	1.0	83.4	12.3	<0.1	<0.1	ND	0.4	3.9	Mg = 0.2 Pb = 2.4
40.	1:1000	1.0	ND	1.0	1.0	85.0	14.0	<0.1	<0.1	ND	0.1	0.9	Fe = 0.5
	1:193	1.26	0.72	1.0	1.0								
41.	1:1000	1.0	1.0	1.0	1.0	83.1	12.3	0.5	0.1	ND	3.7	0.3	Na = 0.09 Si = 0.045
	1:118	1.16	1.16	1.0	1.0								

42.	1:2000	0.77	ND	1.0	1.0	60.5	9.3	<0.1	<0.1	30.0	nil	0.2	K = 0.025 Na = 0.075
43.	1:2000	1.0	ND	1.0	1.0	60.5	9.3	<0.1	<0.1	30.0	nil	0.2	K = 0.025 Na = 0.075
44.	NT <sup>b</sup>					3.7	1.4	3.8	<0.1	ND	11.1	80.0	Ca = 0.2    Mg = 50. Fe = 2.0    Na = 0.5
45.	1:1175	1.0	0.87	1.0	1.0	76.5	10.9	<0.1	0.4	ND	0.6	11.6	Pb = 6.0    Mn = 0.4 Ba = 3.0
46.	1:1070	1.0	0.84	1.0	1.0	79.2	9.0	<0.1	0.3	ND	0.7	10.8	Pb = 5.5    Mn = 0.3 Ba = 2.8
47.	1:1210	1.0	0.85	1.0	1.0	77.0	10.8	<0.1	0.4	ND	nil	11.8	Pb = 6.0    Mn = 0.4 Ba = 3.0
48.	1:320	1.0	ND	1.0	1.0	86.8	12.7	0.2	<0.1	ND	0.3	<0.2	
49.	1:200	1.0	ND	1.4	1.0	73.1	8.3	<0.1	6.5	ND	11.1	1.0	Fe = 0.01
50.	1:400	1.0	1.0	1.0	1.0	46.5	10.4	<0.1	<0.1	ND	43.1	<0.2	
	1:50	0.71	0.71	1.0	1.0								

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%								
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	Oa	Ash	Metals	
51.	1:5500	1.0	.87	1.0	1.0	70.2	10.4	<0.1	<0.1	ND	6.4	13.	Mg = 6.0 Al - 0.6	Ca = 0.045
52.	Cannister	1.0	ND <sup>c</sup>	1.0	1.0	5.0	3.2	<0.1	0.1	ND	19.7	72.	Si = 20.0 Al = 10.0 Fe = 3.0 Mg = 1.0 Ca = 1.0	K = 3.0 Na = 3.0 P = 3.0
	Cannister	1.0	ND	1.0	1.0									
53.	1:150	0.57	0.47	1.0	1.0	87.4	8.0	0.2	<0.1	ND	3.4	1.0	Co = 0.3 Ca = 0.1	
54.	1:4000	1.0	1.0	1.0	1.0	86.6	7.8	0.1	<0.1	ND	2.8	2.7	Co = .9	
	1:1070	1.0	1.0	1.0	1.0									
	1:535	1.0	1.0	1.0	1.0									
	1:340	0.67	0.65	1.0	1.0									
	1:214	0.68	0.62	1.0	1.0									
	1:107	0.80	0.57	1.0	1.0									
	1:81	1.0	0.60	1.0	1.0									
	1:54	1.0	0.51	1.0	1.0									
55.	1:4000	1.0	ND	1.0	1.0	91.6	7.6	<0.1	<0.1	ND	0.8	<0.2	Ca = 0.01	



56.	1:4000	1.2	ND	1.0	1.0	88.5	11.4	<0.1	<0.1	ND	nil	<0.2	
57.	NT <sup>b</sup>					0.3	0.1	<0.1	<0.1	ND	39.6	60.0	Na = 30.0 Ca = 0.2 Zn = 10.0 Fe = 1.0
58.	1:1000	1.0	ND	1.0	1.0	92.3	7.7	<0.1	<0.1	ND	nil	<0.2	
59.	1:26,600	1.0	1.0	1.0	1.0	37.6	5.6	<0.1	0.4	ND	3.4	53.	Mg = 30.0 Ca = 1.5 Fe = 0.5 Al = 0.5 Si = 0.5
60.	1:1000	1.0	ND	1.0	1.0	80.5	13.0	0.3	0.1	ND	6.1	<0.2	
61.	1:1000	1.0	ND	1.0	1.0	82.5	9.6	0.9	1.0	ND	6.0	<0.2	
62.	1:1000	1.0	ND	1.0	1.0	84.6	9.9	1.0	0.9	ND	3.6	<0.2	
63.	1:1000	1.25	1.25	1.0	1.0	80.0	12.3	<0.1	<0.1	ND	7.7	<0.1	
	1:50	1.26		1.0	1.0								
64.	1:8800	1.0	1.0	1.0	1.0	29.8	10.4	0.4	<0.1	ND	38.4	21.	Na = 10. Al = 0.02 Si = 0.1
	1:2000	1.0	1.0	1.0	1.0								
	1:1000	1.0	1.0	1.0	1.0								

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%							
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals
65.	1:1000	1.0	ND <sup>c</sup>	1.0	1.0	62.3	6.9	4.2	0.2	0.1	26.3	<0.2	Ba = 3.2 P = 0.4
66.						76.1	11.8	0.1	<0.1	ND	3.7	8.3	
	1:1000	1.0	ND	1.0	1.0								
67.	1:5000	1.0	ND	1.0	1.0	83.0	11.6	0.4	0.1	ND	4.9	<0.2	
	1:5000	1.0	ND	1.0	1.0								Na = 0.09 Si = 0.045
	1:4000	1.0	ND	1.0	1.0								
	1:50	1.2	ND	1.0	1.2								
68.	1:4000	1.0	ND	1.0	1.0	83.1	12.3	0.5	0.1	ND	3.7	0.3	
69.	1:4000	1.0	ND	1.0	1.0	74.5	7.0	8.0	<0.1	ND	10.5	<0.2	
70.	1:1000	1.0	ND	1.0	1.0	70.4	6.3	7.8	<0.1	ND	15.5	<0.2	
71.	1:10,000	1.0	ND	1.0	1.0	77.8	14.0	5.4	<0.1	ND	2.8	<0.2	
72.	1:10,000	1.0	ND	1.0	1.0	78.0	14.3	5.2	<0.1	ND	2.5	<0.2	
73.	1:10,000	1.0	ND	1.0	1.0	83.2	11.4	0.7	<0.1	ND	4.7	<0.2	

74.	1:4000	1.0	ND	1.0	1.0	78.2	11.5	0.2	0.1	nil	9.8	0.2	Cu = 0.01
75.	1:100	1.0	ND	1.0	1.98	44.9	8.6	10.3	<0.1	ND	36.2	<0.2	
76.	1:100	1.0	ND	1.0	1.77	49.5	9.2	9.3	<0.1	ND	32.0	<0.2	
77.	1:100	1.0	ND	1.0	1.0	69.7	10.6	<0.1	<0.1	<0.1	19.5	0.2	
78.	1:13,100	0.74	.72	1.0	1.0	50.3	3.4	<0.1	<0.1	ND	23.3	23.	Al = 0.02 Mn = 24.8
	1:9000	0.56	ND	1.0	1.0								
	1:6550	0.62	0.56	1.0	1.0								
	1:4920	0.64	0.56	1.0	1.0								
	1:3280	0.74	0.52	1.0	1.0								
79.	1:1280	1.0	ND	1.0	1.0	73.0	7.8	0.3	<0.1	13.6	5.3	<0.2	Mn = 0.01
80.	1:3000	1.0	ND	1.0	1.0	56.4	5.7	<0.1	<0.1	15.6	22.3	<0.2	
81.	1:2000	1.0	ND	1.0	1.0	84.4	12.8	0.2	<0.1	ND	2.6	<0.2	
	1:1500	1.0	ND	1.0	1.0								
	1:1000	1.0	ND	1.0	1.0								
	1:1000	0.72	ND	1.0	1.0								
	1:750	0.72	ND	1.0	1.0								
	1:500	1.0	ND	1.0	1.0								
	1:250	1.0	ND	1.0	1.0								

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.



86.	1:400	1.0	ND	1.0	1.0	85.4	14.1	0.2	0.1	ND	nil	0.2	Ca = 0.04
87.	1:4000	1.0	ND	1.0	1.0	80.0	13.5	0.8	1.5	ND	4.2	<0.2	
88.	NT <sup>b</sup>					77.8	10.9	0.4	0.5	ND	9.3	1.1	Cu = 0.6 P = 0.04
89.	NT					81.3	10.8	<0.1	<0.1	ND	6.8	1.1	Cu = 0.6 P = 0.04
90.	NT					0.3	1.7	5.8	<0.1	ND	59.2	33.	Na = 20.    Cu = 0.2 Zn = 5.     Ca = 0.1
91.	1:8000	1.0	ND	1.0	1.0	83.3	11.4	0.9	<0.1	ND	4.4	<0.2	
92.	1:5000	1.0	ND	1.0	1.0	71.1	10.3	<0.1	<0.1	11.3	7.3	<0.2	
93.	1:5000	1.0	ND	1.0	1.0	78.8	8.7	0.4	0.2	5.5	6.4	<0.2	
94.	1:1000	1.26	ND	1.0	1.0	76.0	16.0	<0.1	0.1	ND	7.9	<0.2	Cr = 0.02 Fe = 0.05
95.	1:300	1.0	0.73	1.0	1.0	85.6	8.1	0.2	0.4	ND	3.2	2.5	Ba = 0.4
96.	1:1000	1.4	ND	1.0	1.0	84.5	13.7	<0.1	<0.1	ND	1.8	<0.2	

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%								
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals	
97.	1:525	1.0	0.82	1.0	1.0	79.4	12.3	<0.1	0.1	ND	1.7	6.5	Pb = 3.0 Ba = 0.6	Ca = 0.18
98.	1:480	1.0	ND <sup>c</sup>	1.0	1.0	86.3	13.5	<0.1	0.1	ND	0.1	<0.2		
99.	1:480	1.0	ND	1.0	1.0	86.5	13.4	<0.1	0.1	ND	nil	<0.2		
100.	1:480	1.0	ND	1.0	1.0	86.2	13.8	<0.1	<0.1	ND	nil	<0.2		
101.	1:480	1.0	1.0	1.0	1.0	81.6	14.0	<0.1	<0.1	ND	4.4	<0.2		
102.	1:480	1.0	1.0	1.0	1.0	86.6	13.4	<0.1	<0.1	ND	nil	<0.1		
103.	1:2800	1.0	1.0	1.0	1.0	87.5	10.7	0.1	0.1	ND	1.1	0.5	Fe = 0.15	
	1:1000	1.0	1.0	1.0	1.0									
	1:500	0.69	0.66	1.0	1.0									
	1:250	0.69	0.63	1.0	1.0									
	1:125	0.78	0.70	1.0	1.0									
	1:625	0.85	0.67	1.0	1.0									
104.	NT <sup>b</sup>					4.0	0.6	<0.1	<0.1	ND	21.4	74.	Na = 20. Zn = 10.	Cu = 3.0
105.	1:480	1.0	ND	1.0	1.0	85.6	13.6	<0.1	<0.1	ND	0.8	<0.2		

106.	1:1000	1.0	ND	1.0	1.0	72.1	9.0	0.5	<0.1	16.9	1.5	<0.2	
107.	1:1000	1.0	ND	1.0	1.0	75.5	10.5	0.4	<0.1	11.0	2.6	<0.2	
108.	NT					71.2	9.1	0.4	<0.1	1.3	18.0	<0.2	
109.	1:150	2.0	ND	1.0	1.0	74.7	11.8	0.2	<0.1	ND	3.3	10.	Ba = 4.0
110.	1:4000	1.29	1.21	1.0	1.0	70.1	11.1	<0.1	0.1	ND	0.7	18.	Ba = 7.2
	1:1050	1.44	1.19	1.0	1.0								
111.	NT					67.2	9.8	5.9	<0.1	0.5	16.6	<0.2	
112.	1:3000	1.0	1.0	1.0	1.0	57.7	8.8	1.1	0.3	ND	nil	33.	Ba = 18.9
113.	1:2760	1.45	.81	1.0	1.0	75.1	12.3	<0.1	0.4	ND	0.2	12.	Ba = 4.8 P = 3.6
114.	1:2080	1.0	1.0	1.0	1.0	73.3	11.8	<0.1	0.1	ND	9.0	5.8	Ba = 0.6 Pb = 3.0
115.	1:6000	0.80	0.77	1.0	1.0	79.2	10.2	0.1	1.0	ND	nil	9.9	Ba = 5.2 Pb = 0.1
	1:1000	1.0	1.0	1.0	1.0								

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%								
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals	
116.	1:3000	1.0	ND <sup>c</sup>	1.0	1.0	63.9	9.0	0.1	0.8	ND	4.2	22.0	Pb = 12. Ba = 8.0	Mn = 0.2 Si = 0.1
117.	1:3000	1.0	ND	1.0	1.0	71.0	8.8	0.1	0.5	ND	3.6	16.	Ba = 2.9 Mn = 0.15	Pb = 3.0
	1:2000	1.0	ND	1.0	1.0									
	1:1000	1.0	ND	1.0	1.0									
	1:750	1.0	ND	1.0	1.0									
118.	1:1000	0.88	ND	1.0	1.0	70.7	9.9	0.1	0.5	ND	3.8	15.	Pb = 4.5 Ba = 2.9 Mn = 0.15	
119.	Canister	1.25	ND	1.0	1.0	3.0	1.2	1.0	0.3	ND	13.5	81.	Mg = 47.9 Fe = 1.0	
120.	1:535	1.43	1.43	1.0	1.0	83.0	12.1	<0.1	1.0	ND	1.6	2.3	Na = 0.6 Si = 0.014	
121.	1:1000	1.0	ND	1.0	1.0	85.4	14.3	0.1	<0.1	ND	0.2	<0.2		
122.	1:10,000	1.57	1.57	1.0	1.0	71.4	12.5	4.4	<0.1	ND	10.3	1.4	K = 0.1 P = 0.4	Ni = 0.05 Mg = 0.03 Ca = 0.03



	1:1000	1.15	ND	1.0	1.0														
	1:400	1.17	1.14	1.0	1.0														
123.	NT <sup>b</sup>					1.0	1.4	4.2	<0.1	ND	20.4	73.	Na = 30. Cu = 3.0						
124.	NT					<0.1	0.6	2.2	<0.1	ND	13.2	84.	Na = 25. Zn = 5.0	Cu = 3.0 Fe = 1.0					
125.	1:156	1.28	1.24	1.0	1.0	80.4	12.5	0.1	<0.1	ND	6.4	0.6	Cu = .5						
126.	NT					0.3	0.3	0.2	0.3	ND	2.9	96.	Mg = 40. Cu = 1.0 Ca = 1.0	Si = 0.3 Al = 0.1					
127.	1:2000	1.0	ND	1.0	1.0	84.8	9.4	0.3	<0.1	ND	5.5	<0.2							
128.	1:3500	1.0	1.0	1.0	1.0	64.8	11.0	0.1	1.7	ND	11.4	11.0	Na = 3.0 Si = 1.0	Al = 0.2					
129.	1:700	1.0	1.0	1.0	1.0	80.9	13.3	0.1	0.1	ND	4.0	1.6	Mn = 0.8 P = 0.64						
130.	1:1000	1.18	ND	1.0	1.0	82.7	11.0	0.4	<0.1	ND	5.9	<0.2							
131.	1:1000	1.0	ND	1.0	1.0	81.1	11.5	1.6	<0.1	ND	5.5	0.3							

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%								
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals	
132.	NT <sup>b</sup>					79.6	9.4	1.2	<0.1	ND	9.8	<0.2		
133.	NT					88.4	10.2	1.2	<0.1	ND	0.2	<0.2		
134.	NT					83.2	11.1	1.1	1.2	ND	3.4	<0.2		
135.	1:1000	1.0	ND <sup>c</sup>	1.0	1.0	82.5	10.9	3.8	<0.1	ND	2.8	<0.2		
136.	1:8000	1.0	ND	1.0	1.0	77.9	13.2	2.9	<0.1	ND	6.0	<0.2		
	1:6000	1.0	ND	1.0	1.0									
	1:4000	1.0	ND	1.0	1.0									
	1:2000	1.0	ND	1.0	1.0									
	1:1000	1.0	ND	1.0	1.0									
	1:500	1.0	ND	1.0	1.0									
137.	1:8000	1.0	1.0	1.0	1.0	66.7	10.6	1.5	<0.1	7.4	13.2	0.6	Pb = 0.24      Cu = 0.03 Si = 0.06      Al = 0.018 Ni = 0.042	
	1:110	1.28	1.0	1.0	1.1									
138.	1:1000	1.0	ND	1.0	1.0	78.0	10.8	5.5	<0.1	ND	5.7	<0.2		
139.	1:1000	1.28	ND	1.0	1.0	78.4	10.6	6.3	<0.1	ND	4.2	0.5		

140.	1:1000	1.0	ND	1.0	1.0	79.9	10.9	5.8	<0.1	ND	3.4	<0.2	
141.	1:1000	1.0	ND	1.0	1.1	80.3	10.2	3.7	<0.1	ND	5.8	<0.2	
142.	NT					76.5	12.1	<0.1	2.5	ND	0.2	8.7	Ca = 3.6
143.	NT					61.2	8.0	<0.1	1.8	ND	8.0	21.	Ca = 12.
144.	1:1000	1.0	0.79	1.0	1.0	82.2	12.0	<0.1	1.2	ND	nil	4.8	Ca = 2.0
145.	NT					68.8	11.4	0.2	2.0	0.1	12.8	4.7	Mn = 2.0
146.	NT					66.6	11.4	<0.1	1.8	18.0	<0.1	2.9	Mg = 1.0
147.	NT					1.2	0.7	15.3	7.3	ND	37.3	38.	K= 30.
148.	1:4000	1.0	ND	1.0	1.0	61.2	9.7	<0.1	<0.1	nil	28.8	0.3	K = 0.03 Na = 0.075
149.	1:1000	1.24	1.0	1.0	1.0	76.3	8.9	<0.1	<0.1	ND	5.9	8.9	Pb = 5.4 Si = .45
150.	1:1000	1.0	ND	1.0	1.0	86.4	8.4	<0.1	<0.1	ND	5.2	<0.2	

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%								
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.		Ash	Metals	
151.	1:65	1.0	0.84	1.0	1.0	77.3	8.7	<0.1	<0.1	ND	9.1	4.9	Pb = 03.0 Si = 0.25 Cu = 0.25	Ni = 0.05
152.	NT <sup>b</sup>					37.3	8.6	<0.1	0.3	ND	24.8	29.	Mg = 12. Ca = 0.6	Si = 0.3 Al = 0.15
153.	1:1000	1.0	1.0	1.0	1.0	77.2	8.3	<0.1	<0.1	12.5	2.0	0.2		
154.	NT					52.6	10.0	0.1	0.5	ND	7.8	29.	Mg = 18. Ca = 0.9	Al = 0.3
155.	NT					31.4	8.2	<0.1	0.4	0.1	30.9	29.	Al = 12. Na = 0.15	
156.	1:4000	1.0	1.0	1.0	1.0	90.4	8.1	0.4	<0.1	ND	0.5	0.6		
157.	1:2500	1.0	1.0	1.0	1.0	78.6	9.8	0.1	0.3	ND	2.2	9.0	Ca = 0.4 Pb = 6.0	
	1:780	1.0	1.0	1.0	1.0									
158.	1:3750	1.0	1.0	1.0	1.0	60.4	7.2	<0.1	<0.1	0.4	nil	32.	Si = 14.6 P = 0.36	
159.	1:1800	1.0	1.0	1.0	1.0	67.6	10.1	<0.1	0.5	ND	2.8	19.	Pb = 13.3 Ca = 1.0	

160.	1:9800	1.0	1.0	1.0	1.0	78.8	11.8	0.5	1.9	ND	nil	7.3	Ca = 3.2 Na = 0.04	
	1:4000	1.0	1.0	1.0	1.0									
	1:1600	1.0	1.0	1.0	1.0									
161.	1:21,000	1.0	1.0	1.0	1.0	31.0	6.5	<0.1	0.4	0.1	27.0	35.0	Mg = 17.5 Zn = 15.0	Si = 2.5
162.	NT					10.5	2.2	2.2	<0.1	ND	24.1	61.	Na = 30. Zn = 3.0	Cu = 3.0
163.	NT					10.6	1.5	3.6	<0.1	ND	26.3	58.	Mg = 20. Na = 3.0	Fe = 4.0 Ca = 15. Cu = 3.0
164.	1:850	0.86	0.85	1.0	1.0	78.3	12.5	<0.1	0.6	ND	5.5	3.1	Na = 0.6 Cu = 0.45	P = 0.18 Mg = 0.09
165.	NT					37.6	5.6	<0.1	0.1	ND	2.7	54.	Mg = 2.7 Cu = 2.7	Ca = 1.6 Si = 1.1
166.	1:1250	1.0	1.0	1.0	1.0	83.1	12.9	<0.1	0.9	ND	0.5	2.6	Pb = 0.03 Na = 1.4	
167.	1:1000	1.23	ND <sup>c</sup>	1.0	1.0	80.1	9.4	0.1	<0.1	ND	10.4	<0.2		

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%								Metals	
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash			
168.	1:185	1.28	1.18	1.0	1.0	84.5	9.9	<0.1	<0.1	ND	4.8	0.8	Cu = 0.24 Mn = 0.24		
169.	1:480	1.0	1.0	1.0	1.0	70.6	8.1	<0.1	0.1	0.1	18.9	2.3	Zn = 0.8 Pb = 0.6	Mg = 0.2	
170.	1:1420	1.0	1.0	1.0	1.0	77.0	10.4	1.8	0.1	ND	7.0	3.7	Mg = 1.6 Ca = 0.16		
171.	NT <sup>b</sup>					2.7	0.7	<0.1	0.3	ND	16.3	80.	Na = 20. Zn = 10. Ca = 5.0	Si = 4.0 Al = 2.0 B = 1.0 Fe = 1.0	
172.	NT					5.1	0.8	<0.1	0.1	ND	21.0	73.	Zm = 20. Ma = 10. Ca = 10.	Si = 5.0 Al = 3.0 B = 1.0	
173.	1:1000	1.0	ND	1.0	1.0	70.3	9.2	2.4	<0.1	0.1	18.0	<0.2			
174.	1:1000	1.0	ND	1.0	1.0	82.1	13.3	0.4	<0.1	ND	4.2	<0.2			
175.	1:8000	1.0	ND	1.0	1.0	74.2	13.3	7.1	<0.1	ND	5.4	<0.2			
176.	1:5000	1.19	ND	1.0	1.0	90.6	7.4	0.5	0.7	ND	0.8	<0.2			

177.	1:685	1.14	1.14	1.0	1.0	83.8	8.3	0.4	0.7	ND	4.9	1.9	Mg = 0.6 Na = 0.4	Si = 0.04
178.	1:1000	1.0	ND	1.0	1.0	64.8	9.5	1.6	<0.1	21.9	2.2	<0.2		
179.	1:1000	1.0	ND	1.0	1.0									
180.	1:800	1.0	ND	1.0	1.0	74.6	12.6	7.0	<0.1	ND	5.8	<0.2		
181.	1:2000	1.0	ND	1.0	1.0	77.2	8.3	<0.1	<0.1	12.5	2.0	<0.2		
	1:1500	1.0	ND	1.0	1.0									
	1:1000	1.0	ND	1.0	1.0									
	1:750	1.0	ND	1.0	1.0									
	1:500	1.0	ND	1.0	1.0									
	1:250	1.17	ND	1.0	1.0									
182.	1:1000	1.26	ND	1.0	1.0	61.1	8.2	<0.1	<0.1	9.1	21.6	<0.2	Pb = 0.6	P = 0.1
183.	1:1000	1.22	ND	1.0	1.0	81.7	11.7	<0.1	<0.1	ND	5.0	1.6		
184.	1:1000	1.19	ND	1.0	1.0	71.3	13.3	6.2	<0.1	nil	9.2	<0.2		
185.	1:1000	1.0	ND	1.0	1.0	71.9	12.8	6.5	<0.1	nil	8.8	<0.2		
186.	1:20,000	1.0	ND	1.0	1.0	72.9	12.5	6.0	<0.1	ND	8.6	<0.2		

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## TEST RESULTS AND ADDITIVE ANALYSIS (continued)

Add. No.	Test dose	Pollutant ratio				Additive composition, wt%							
		Total part. ratio	Carbon part. ratio	SO <sub>x</sub> ratio	NO <sub>x</sub> ratio	C	H	N	S	Hal.	O <sup>a</sup>	Ash	Metals
187.	1:20,000	1.0	ND	1.0	1.0	79.3	10.8	3.5	<0.1	ND	6.4	<0.2	Mn = 0.25
188.	1:20,000	1.0	ND	1.0	1.0	78.8	9.1	1.0	<0.1	5.6	5.5	<0.2	
189.	1:20,000	1.0	ND	1.0	1.0	84.8	13.1	0.1	<0.1	ND	1.5	0.5	
190.	1:1000	1.0	ND	1.0	1.0	81.4	11.2	0.1	0.3	ND	6.7	0.3	
191.	1:1000	1.0	ND	1.12	1.0	74.0	10.9	4.3	9.1	ND	1.7	<0.2	
192.	1:1000	1.0	ND	1.0	1.0	77.2	11.3	1.6	3.5	ND	6.4	<0.2	
193.	1:1000	1.0	ND	1.0	1.0	70.8	10.5	1.5	<0.1	ND	17.2	<0.2	
194.	1:1000	1.0	ND	1.0	1.0	65.9	9.5	1.5	2.6	ND	20.5	<0.2	
195.	1:1000	1.0	ND	1.0	1.0	65.8	5.9	8.6	0.1	ND	19.6	<0.2	Ca = 10.
196.	1:4000	1.0	ND	1.0	1.0	87.3	11.9	<0.1	0.1	ND	0.7	<0.2	
197.	1:5000	1.0	1.0	1.0	1.0	59.6	8.9	0.1	1.7	ND	8.7	21.	
198.	1:1000	1.0	ND	1.0	1.0	76.4	12.9	<0.1	<0.1	0.1	10.6	<0.2	
199.	1:1000	1.0	ND	1.0	1.0	90.2	8.2	0.3	0.3	ND	0.8	0.2	



200.	1:1000	1.0	ND	1.0	1.0	91.8	8.2	<0.1	<0.1	ND	nil	<0.2		
201.	1:2000	1.0	1.0	1.0	1.0	76.2	11.7	<0.1	0.2	ND	2.6	9.3	Ba = 4.5 Fe = 0.27	P = 0.9
	1:1500	1.0	0.76	1.0	1.0									
	1:1000	1.0	0.81	1.0	1.0									
	1:750	1.0	0.88	1.0	1.0									
	1:500	1.0	1.0	1.0	1.0									
	1:185	1.33	1.0	1.0	1.0									
202.	1:1500	1.0	ND	1.0	1.0	78.2	7.4	1.2	<0.1	0.2	12.0	1.0	Mn = 0.5	
	1:1000	0.82	ND	1.0	1.0									
	1:500	1.0	ND	1.0	1.0									
	1:370	1.17	ND	1.0	1.0									
	1:185	1.59	1.0	1.0	1.0									
203.	1:500	1.0	1.0	1.0	1.0	80.7	10.4	0.3	1.4	ND	6.3	0.9	Fe = 0.4 Sn = 0.05	
	1:302	1.0	ND	1.0	1.0									
	1:151	1.0	ND	1.0	1.0									
204.	1:4000	1.0	ND	1.0	1.0	75.3	11.1	<0.1	<0.1	nil	13.4	0.2	Fe = 0.06 Cr = 0.02	Pb = 0.01
205.	1:4000	1.0	ND	1.0	1.0	79.2	7.1	0.5	<0.1	3.2	10.0	<0.2		
206.	1:4000	1.0	ND	1.0	1.0	75.0	8.8	0.2	<0.1	8.7	7.1	0.2		

<sup>a</sup>This value was determined by difference.

<sup>b</sup>NT = Not tested.

<sup>c</sup>ND = Not determined.

## BIBLIOGRAPHY

1. Wasser, J. H., R. P. Hangebrauck, and A. J. Schwartz. Effects of air-fuel stoichiometry on air pollutant emissions from an oil-fired test furnace. JAPCA. 18(5):332-37. May 1968.
2. Wasser, J. H., G. B. Martin, and R. P. Hangebrauck. Effects of combustion gas residence time on air pollutant emissions from an oil-fired test furnace. In: Proc. 1st National Oil Fuel Institute New and Improved Oil Burner Equipment Workshop. Linden, N. J. Sept. 17-18, 1968. NOFI Tech. Publ. 106 Ed. pp. 110/1 110/13.
3. Riggs, R. J., T. J. Wilkison, and H. R. Wolfe. Combustion improvers for fuel oils. Ethyl Corporation Publication. 1966.
4. Arapahoe Chemical Catalog. Arapahoe Chemicals. Division of Syntex Corp. Boulder, Colo.
5. "Ethyl" Combustion Improver Literature. Ethyl Corporation. New York.
6. Litton Systems, Inc. Preliminary air pollution survey of manganese and its compounds: a literature survey. Oct. 1969. Contract No. PH 22-68-25, Air Pollution Control Office. Raleigh, N. C. Pub. No. APTD 69-39.
7. Litton Systems, Inc. Preliminary air pollution survey of iron and its compounds: a literature survey. Oct. 1969. Contract No. PH 22-68-25, Air Pollution Control Office. Raleigh, N. C. Pub. No. APTD 69-38.
8. Sax, N. I. Dangerous Properties of Industrial Materials. Reinhold Publishing Corporation. New York. 1963.
9. Howekamp, D. P., and M. H. Hooper. Effects of combustion-improving devices on air pollutant emissions from residential oil-fired furnaces. Air Pollution Control Office. Cincinnati, Ohio. 1970.
10. Howekamp, D. P. Flame retention effects on air pollution. NOFI Annual Convention. Atlantic City, N. J. June 1970.
11. Martin, G. B. Use of Fuel additives and combustion improving devices to reduce air pollution emissions from domestic oil furnaces. Air Pollution Control Office. Cincinnati, Ohio. 1970.

12. Colborne, W. G. Performance of intermittently fired oil furnaces. Heat, Piping, and Air Cond. p. 147-150. April 1957.
13. Chass, R. L. et al. A joint project, emissions of oxides of nitrogen from stationary sources in Los Angeles County. Report No. 1. p. 24-34. Los Angeles County Air Pollution District. Los Angeles. February 1960.
14. Lisle, E. S., and J. D. Sensenbaugh. The determination of  $\text{SO}_3$  and acid dew point in flue gases. Combustion, 36:12-16. January 1965.
15. Shell Development Company Analytical Department. Determination of sulfur dioxide and sulfur trioxide in stack gases. Emeryville, Calif. 1959.