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COMPOSITION AND METHOD FOR REDUCING AIR POLLUTANTS

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U.S. Cl. 44—4 32 Claims

ABSTRACT OF THE DISCLOSURE

A novel manganese complex is described. It is useful in controlling the combustion of fuels and to reduce the amounts of resulting noxious fumes and smoke. Among the noxious fumes and smokes reduced are sulfur trioxide and dioxide, sulfuric acid, carbon monoxide, the nitrogen oxides, unburnt hydrocarbons, carbon particles, and large ash agglomerates. The manganese complex is oil-soluble and is directly admixed when used with liquid fuels. It is dissolved and sprayed upon solid fuels. The manganese complex is useful for improving combustion in both internal and external combustion arrangements. Added benefits from the use of the novel manganese complex in fuels are reduction of combustion deposits, improved fuel utilization, better flame configuration and more uniform and higher flame temperatures. Specific details of the manganese complex and methods for making and using same are set forth in the specification.

This is a continuation-in-part of my application Ser. No. 567,398 filed July 25, 1966, and now abandoned.

This invention relates to manganese complexes and to compositions and methods utilizing such complexes for improving and modifying the combustion of fuels. More particularly, the present invention relates to a method and composition for reducing the amount of noxious particles and gases which result from the improved combustion of fuels containing this complex.

The combustion of most modern industrial fuels leads, in addition to the intended production of energy, to the gaseous products of combustion such as carbon dioxide and water and the unintended production of pollutants which include noxious by-products such as carbon monoxide, smoke, sulfur oxides, sulfuric acid, nitrogen oxides, unburnt hydrocarbons, acid smut, particulate matter, ash and miscellaneous gases and oxides.

Carbon dioxide results from the proper and complete combustion of the conventional carbonaceous fuels of fossil or woody origin. The noxious by-products result from improper combustion impurities in the fuels, and residues of incombustibles.

Carbon monoxide, unburnt hydrocarbons and carbon particles in the exhaust gases are particularly noxious and are major health threats among air pollutants resulting from fuel combustion. All three result from improper combustion caused by such factors as insufficient air supply, too low flame-temperatures and too slow flame-propagation. Carbon monoxide is a well known toxic agent. Unburnt hydrocarbons and carbon particles are dangerous air pollutants inasmuch as they provide major sources of nucleii for smog formation as well as being irritants in their own right.

The other noxious fumes result from the reactions in the flames, acting on either the nitrogen in the combustion air or the impurities in the fuels being burnt. The

nitrogen oxides are commonly formed in small amounts within the flame according to the reaction:

$$N_2 + O_2 \rightarrow 2NO$$

The reaction is temperature dependent, and according to some authorities, involves free radical mechanisms.

The sulfur oxides result from the oxidation of elemental sulfur or other sulfur containing moieties often found as impurities suspended, dissolved or distributed in fuels such as oil, coal or L.P.G. Upon initial oxidation, SO_2 usually is formed. It is a toxic gas having a distinctly objectionable odor. Upon further oxidation SO_3 is formed. This, in the presence of water, forms sulfuric acid which is extremely toxic and irritating to living matter and is generally corrosive to structural materials.

Other noxious pollutants include fly ash and smoke which consists of unburned fuel as well as the carbonates and oxides of those metals which are present in varying amounts as fuel impurities. Sodium, potassium, calcium magnesium and vanadium are the most common of such metals. Their carbonates and oxides are the major components of fly ash and smoke.

Most commercially used fuels, ranging from coal through fuel oils to gasoline, contain fuel additives for varying reasons. Choice of additives depends on the source of the fuel, the type of equipment in which it is used, characteristics of the fuel, and the economics of the specific situation. Most fuel additives heretofore have been compounded to stabilize the fuel, to control utilization rates, to control ash composition or adherence, or to modify flame characteristics.

Some improvement in combustion rates have resulted from the use of previous additives and better control of carbon monoxide, unburnt hydrocarbons and carbon particles in the exhaust or stack gases has resulted from their use. However, these improvements have not resulted in the complete abatement of the problem. There is room for improvement.

In the case of the nitrogen oxides, it has been proposed to pass the exhaust gases through catalyst beds where these noxious gases are reacted and reduced to nitrogen, hopefully without formation of other noxious by-products. With regard to sulfur-containing fuels, it has, prior to the present invention, been proposed to control the amount of the sulfur oxide gases issuing in exhaust gases by pretreatment of the fuels to limit the amount of free and combined sulfur therein. However, the costs involved have made such pretreatments generally uneconomical for commercial use in the absence of specific requirements imposed by anti-pollution laws.

I have discovered a novel composition which, when added to fuels, provides good combustion control and unexpectedly provides a substantial reduction in the noxious fume content of exhaust gases from the burning of fuels in internal and external combustion.

The present invention resides in novel manganous-amine complexes, their preparation, compositions containing them, the use of such complexes and compositions as additives to fuels, and the fuels containing such additives.

The manganous-amine complexes of the present invention, when added to solid or liquid fuels, such as coal and oil, have been found to reduce sulfur oxides, and particularly the sulfur trioxide content, of the stack gases as much as 50% and, often if added in sufficient amount, by even higher percentages.

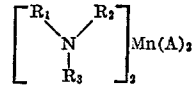
Further, use of the manganous-amine complexes of this invention also reduces the emission of smoke, nitrogen oxides, unburnt hydrocarbons and carbon particles. The exact mechanism by which the rates and types of these noxious emissions are altered is not completely understood. The addition of the amine complex has been

noted to raise the temperature of the flame by at least 50° C. and up to more than 300° C. as measured by optical pyrometry. Similarly the rate of flame propagation and the thermal conductivity are also increased. This has been noted in both external and internal combustion systems. As a result, in powerhouse boilers, the flame configuration is significantly shorter and brighter; and in gasoline engines, fuels of normally lower octane rating can be used without knocking or power loss.

Most significant or at least most noticeable is the marked reduction in visible smoke when the fuels of this invention are substituted for conventional fuels. This smoke reduction has been noted in oil-burning power installations; coal burning furnaces; diesel engines, stationary and motive; gasoline engines and gas turbines. Since smoke is the most noticeable pollutant, reduction in the amount and density of the smoke, reduces the frequency and intensity of air pollution complaints. The reduction of smoke density is an indication of significant reduction in the amount of unburnt carbon particles and unburnt hydrocarbons emitted into the atmosphere. This has been borne out in specific instances where measurement of smoke density and the amounts of unburnt carbon and hydrocarbons have been made before and during the use of the treated fuels.

When compared to conventional fuels, the combustion of fuels containing the manganous-amine complex of this invention also reduces the amounts of nitrogen oxide in the exhaust gases. The manganous-amine complex during combustion appears to provide a subsidiary oxygen atom scavenging reaction which alters or blocks, at least one of the nitrogen oxide reaction rates, to a point where, instead of nitrogen oxides being formed in usual amounts, the nitrogen is released in molecular form. It should be recalled that the nitrogen oxides are the prime eye irritants in common smog resulting from gasoline and diesel engine emissions. On such engines, fuels according to this invention emit less nitrogen oxides.

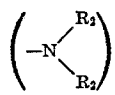
The manganous-amine complex of my invention may be represented by the formula:



where R_1 is selected from the group consisting of saturated and unsaturated, substituted and unsubstituted, aliphatic radicals containing from 1 to 22 carbon atoms, inclusive, and $-(CH_2CH_2)_xH$, where x is an integer having a value of from 1 to 5; R_2 is selected from the group consisting of hydrogen and saturated and unsaturated, substituted and unsubstituted aliphatic radicals containing from 1 to 22 carbon atoms, inclusive, and

$$-(CH_2CH_2O)_xH$$

where x is an integer having a value of from 1 to 5; R_3 is chosen from the group consisting of hydrogen, saturated and unsaturated, substituted and unsubstituted aliphatic radicals containing from 1 to 22 carbon atoms inclusive; $-(CH_2CH_2O)_xH$, where x is an integer having a value of from 1 to 5 and



and A is an inorganic or organic manganous salt-forming anion selected from the group consisting of chloride, phosphate and fatty acid carboxylates having from 1 to 22 carbon atoms, inclusive.

Chloride and phosphate are useful inorganic anions. Among the organic anions, the carboxylates from the acetate to the tallate are preferred.

Inorganic manganous salts or lower carboxylates manganous salts are hydrated, and to facilitate the formation of the manganous-amine coordination complex, it is preferred to dehydrate these salts prior to reacting them with the amines to form the complexes of this invention.

The novel complexes of this invention may be formed by reacting anhydrous manganous salt with amines. The reaction may be carried out by adding the salt to the liquid amine or to a mutual solvent for the amine and the final manganous-amine complex. Liquid alkanols including isopropanol; paraffin hydrocarbons such as "neutral oil" or light fuel oil; aromatic solvents such as toluene, cresylic acid or xylene; are suitable solvent and reaction media. The liquid amines are excellent solvents for the complex and additionally it is often desirable to have an excess of amine present, preferably a long chain amine or the one used to form the complex. If halogenated hydrocarbons are used as reaction media, it is preferred that they be removed prior to admixture of the complex to the fuel, since such materials are pollutants.

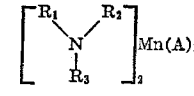
Among the most suitable amines for forming the manganous-amine complexes which will reduce the noxious content of exhaust gases are those having a nitrogen content of at least 1% by weight. Primary, secondary and tertiary alkyl and aralkyl amines are generally suitable for forming such complexes as well as multiple amines such as the diamines and the tetramines. Certain tertiary amines because of steric hindrance are very slow in reacting with the manganese salts, but the final complexes formed are functionally equivalent to the other more rapidly formed complexes. Some relationship between the nitrogen content of the amine and sulfur and nitrogen oxide reduction by the complex has been noted. The amine used to form the complex should have at least 1% by weight of amine nitrogen. but preferably amines of higher of higher nitrogen content should be used.

Among amines which form suitable complexes with anhydrous manganous salts are monoethenolamine, methylamine, diethylamine, triethanolamine, propylamine, N,N-diethenol, laurylamine, N,N-diethenolamine, soyalamine, diethylamine, triethenolamine, propylamine, benzylamine, and a mixture of tertiary alkyl primary amines marketed under the trademark Primene 81 R (Rohm & Haas Corporation).

The manganous-amine complexes of this invention have been found to have an absorbance band in the region of 1410 mμ in the near infrared possibly resulting from the strong ligand field around the central manganous atom. These manganous-amine complexes are all strongly colored with reddish-brown to almost black shades predominating. In very dilute solution the dominant color appears to be red, but sometimes greenish tints by transmitted light are found with the manganous ethanolamine complexes.

The manganese amine complexs of this invention are definite compounds. However, the exact configuration of these complexes is uncertain. In certain characteristics they appear to be coordination complexes possessing strong ligand fields around the central manganese atom; in other characteristics they resemble "charge-transfer complexes" as described by Jaffe and Orchin "Theory and Applications of Ultraviolet Spectroscopy" John Wiley and Sons, Inc., 1962, pages 256, 271, 508, 531, 532, and 588, but such characterizations are not mutually exclusive.

By means of the mole ratio method, the complexes conform to the formula:



Spectral measurements at wave lengths between 400 mμ and 600 mμ show that the mole ratio of the amine to manganese is 2:1. Similarly when the complexes are made from oil insoluble manganese salts, such as the anhydrous acetate; and amines, the ratio of the amine to the manganese is also 2:1. Such manganese salts are not directly soluble in the amine, and they must be brought into the solution through the formation of the complex. The minimum number of moles of amine required to dissolve such

salts is 2 moles, thus bearing out the characteristic molecular identity of the complexes as compounds

The visible and ultraviolet spectra of the manganese complexes of this invention show a continuous absorption in the range of 200 to 600 mμ. In these regions no specific absorption areas are indicated. The broad band absorption is now recognized as characteristic of the spectra of "charge-transfer" complexes. This broad band absorption tends to mask details of specific ligand field spectral regions which are characteristic of certain 4-coordinate complexes.

In cases of the complexes of this invention, it is postulated that two of the coordinate positions are occupied by the manganous organo-salt anion and two coordinate positions are occupied by the amine radicals.

In preparing the complexes of this invention, it is preferred that manganese be in the form of an anhydrous salt of a carboxylate of less than 5 carbon atoms. When the anhydrous salts are treated with the amine, the reaction starts slowly. However, when the temperature is elevated above 80° F. and preferably to about 125° F. (ca. 50° C.), the reaction becomes more rapid, and the color of the manganese amine complex is noted on the surface of the solid salt or in solution when the salt is dissolved in an organic solvent. At higher temperatures and with stirring the reactions proceed more rapidly.

With the long chain carboxylates of manganese, dehydration of the manganous salt is not neccessary. Such organic molecules are not hydrated and are readily soluble in organic compounds. In organic solution the reaction with the long chain carboxylates proceeds readily at normal temperatures.

When solutions of these manganous-amine complexes in alcohol are diluted with water, the complexes precipitate as red-brown to black flocculent powders. These powders, when dried, are light-stable and heat-stable. These powdered complexes can be redissolved in solvents for the complex such as isopropanol or toluene. The redissolved material shows the same IR absorption and the same strong solution colors in the visible range which are characteristic of the manganous-amine complexes of this invention.

The manganous-amine complexes, as formed or as redissolved, when introduced into the fuels, are active in reducing the noxious fume content of the combustion gases. When the complex, at concentrations as low as 1 part per million manganese, as the manganous-amine complex, is added to fuel oil it has been observed to reduce the sulphur oxide content of stack gases resulting from the combustion of the fuel oil in commercial boiler installations. At higher complex concentrations the sulfur oxide concentrations of stack gases in oil-burning commercial boiler and power plant installations have been reduced 50% and more. At levels above 1 part per mililon of manganese, as the complex, the compositions of this invention are effective in improving the combustion efficiency in all grades of fuel oils including residual oils such as Bunker C and comparable grades.

At such leveds not only is there a decrease in sulfur trioxide content but increases in flame temperatures, and shorter brighter flames have been noted with all commercial fuel oil grades. Smoke measurements indicate that a significant smoke reduction, particularly of dark and opaque components results with as little as one part per million of the manganese in the form of the manganous-amine complex of this invention. Analysis of the smoke and other emitted fumes shows increased carbon dioxide contents coupled with lower concentrations of carbon monoxide and unburnt carbon andhydrocarbon contents as compared to fuels free from the additive of this invention.

In internal combustion engines, operating on either gasoline or diesel fuels, reduced smoke has been noted as well as a reduction in the amounts of emited nitrogen oxides when the complexes of this invention are introduced into the fuels. Sulfur oxides are seldom a problem in gasoline engines because the commercial refining operations eliminate, in significant amounts, all forms of sulfur from the gasoline. However, sulfur oxides are encountered in diesel engine exhausts.

The nitrogen oxides are formed in the internal combustion engines probably because of the high pressures and high temperatures during combustion within the cylinders of such engines. The nitrogen oxides are produced in such quantities, that coupled with the number of vehicles on the road a serious public health problem is created from nitrogen oxide emission in engine exhausts. When the manganous-amine complexes of this invention have been added in amounts of at least one part per million of manganese as the complex, the nitrogen oxide in the emitted exhaust is substantially reduced.

In the internal combustion engines, due to some unknown mechanism resulting from the presence of the complexes of this invention, a noticeable improvement in flame propagation within the engines has been noted. In gasoline engines this has resulted in reducing the total amount of lead required to prevent knocking in an engine having a given compression. In diesel engines this improved flame propagation rate makes less critical the injection pressures and combustion chamber configurations.

In powerhouse installations using coal as the fuel, when the manganous-amine complex of this invention has been added to the coal in amounts ranging between 8 and 15 parts per million, a reduction in the sulfur oxide content emitted in the stack gases has been noted. In addition, examination of the firebox, boiler tubes and accessory installations, has shown that previously noted accumulations of moist or gummy carbon deposits have disappeared. It is believed that these deposits consist of long chain hydrocarbon sulfonates and sulfates dissolved or suspended in sulfuric acid. During the combustion the higher sulfur oxide, trioxide reacts with some of the vaporized coal components to form these gummy by-products as well as sulfuric acid. This results in a sticky, moist material which deposits at distal portions of the firebox, on the boiler tubes and in the lower reaches of the stacks. These extremely corrosive deposits not only reduce the efficiency of the equipment by interfering with heat transfer, but they also lead to costly breakdowns and shutdowns. As noted above, when the complexes of this invention have been used in conjunction with the coal for appreciable time, i.e. at least a week, the character of the deposits is changed. It is no longer gummy or adherent to the heat transfer surfaces or linings of the equipment. In addition, checking in the bag filters and electrostatic precipitators shows that these deposits are moved out of the combustion chambers and accessory hot gas areas. When the additive of this invention is used for at least two months, the internal surfaces previously coated with the acidic gummy deposits are freed from deleterious deposits.

When used in connection with fuel oil, a concentrate of the complex prepared by dissolving the complex in a solvent and/or a small portion of fuel oil, is added to the major portions of the fuel oil. Such concentrates form solutions in the fuel oil. Such solutions are stable for extended periods of time at the preheater temperatures commonly used prior to combustion. Generally the amount of the complex in the concentrate can be adjusted so that one gallon of the concentrate added to amounts of fuel oil up to 15,000 gallons to yield the desired concentrations of the complex in the final fuel. At least 1 part per million of manganese, as the manganous-amine complex is desirable, and the economics indicate that 1½ parts per million are preferred.

To facilitate the mixing of the complex through the fuel oil, various surfactants may be included in the concentrate. Viscosity-reducing compounds may also be added. Excesses of the amine have proven excellent viscosity-reducing agents for this purpose. Similarly low molecular

weight alkenols, neutral oils or mixtures thereof may be added to the concentrate in order to speed the spreading of the complex through the large volume of fuel oil. Aromatic solvents such as cresylic acid are also useful to reduce the viscosity of the fuel oils.

When used in connection with gasoline, kerosene and light oils of the diesel grade, it is preferred to use the amine complexes of this invention dissolved in a light petroleum distillate fraction known as "neutral oil." To this solution it is preferred, but not necessary, to add an excess of one of the amines used for forming the complex. It appears that this slight excess of amine together with the manganous-amine complex improves the nitrogen oxide ratio with the treated fuel. It also appears that when such fuels, particularly kerosene to which the manganous-amine of this invention has been added, is burned in gas turbines, that reduction of smoke results.

The following examples illustrate the preparation of the manganous-amine coordination complexes upon which this invention is based, the preparation of concentrated compositions containing these manganous-amine coordination complexes, fuel compositions containing these complexes and the method of reducing the noxious fume content in the exhaust gases by the combustion of fuels containing the manganous-amine coordination complexes of this invention under various conditions. The examples are merely illustrative of the compositions and methods. They are presented without any intention that the invention will be limited thereto. All recognized equivalents of the materials mentioned are specifically intended for inclusion within the scope of the invention.

Example 1

Anhydrous manganous acetate, $Mn(OOC.CH_3)_2$, 0.173 gram, was triturated in 0.178 gram of dimethylethanolamine. To this trituration was added 2 milliliters of dichloroethane and the resultant mixture was heated to 55° C. on a hot plate and maintained at this temperature for 10 minutes. All the solid manganous acetate dissolved and the resultant solution was observed to be deep red-brown in color, indicating the formation of a manganous-amine complex. When the solution was diluted with 10 volumes of dichloroethane per volume of solution, the resultant solution exhibited a greenish color when viewed in thin section by transmitted light. By infrared spectrometry, the solution exhibited an absorbance at 1410 mμ.

Example 2

The trituration and solution procedure set forth in Example 1 was conducted with neutral oil substituted for the dichloroethane of Example 1 both as the solvent and the diluent.

Example 3

Anhydrous manganese acetate, $Mn(OOC.CH_3)_2$, 0.173 gram, was triturated with 0.356 gram of dimethylethanolamine and warmed for 15 minutes at 55° C. with constant stirring. All of the manganous acetate dissolved in the excess amine during this period and formed the deep red manganous-amine complex which exhibited absorbance at 1410 mμ.

Example 4

The procedure according to Example 2 was followed using anhydrous manganese chloride ($MnCl_2$) in place of the manganous acetate. A deep red to black solution of the manganous-amine complex was formed was found to be greenish in dilute solution when viewed by transmitted light.

Example 5

Anhydrous maganous chloride 0.126 gram was triturated with 0.720 gram of N,N-diethoxy soya-amine (molecular weight 360) (Sipenol 1 SO2 manufactured by Alcolac Chemical Corporation.) Two milliliters of dichloroethane and the mixture were heated for 15 minutes at 55° C. during which time all of the manganous chloride had dissolved and formed the maganous-amine complex as evidenced by the deep red-brown color of the solution. This complex upon dilution exhibited a reddish color by transmitted light and showed absorbance at 1410 mμ by infrared spectroscopy.

Example 6

Anhydrous maganous acetate 0.173 gram was triturated with 1.44 gram of N,N-diethoxy soya-amine (of Example 5) and heated to 60° C. The reaction appeared completed within 45 minutes and yielded a deep red solution of the manganous-amine complex in the excess of amine. This solution of the complex showed absorbance at 1410 mμ.

Example 7

Anhydrous manganese chloride, 0.126 gram was triturated with 1.44 gram of N,N-diethoxy soya-amine and was heated at 55° C. The reaction reached completion within 10 minutes and yielded a deep red solution of the manganous-amine complex in the excess of amine which showed IR absorbance at 1410 mμ.

Example 8

Manganous nonanoate $[CH_3(CH_2)_7COO]_2Mn$, 0.369 gram was triturated with .720 gram of diethoxy soya-amine and 2 milliliters of neutral oil and warmed to 30° C., at which temperature the reaction started as was evidenced by the formation of the characteristic deep red color in the solution. The reaction was complete within 5 minutes, and the resulting deep red solution showed infrared absorbance at 1410 mμ.

Example 9

Manganous tallate, 0.920 gram (prepared from the tall oil acids (Circa 22 carbon atoms) and standardized at 6% manganous manganese under the trade name Witall by Witco Products) was triturated at 30° C. for 5 minutes with 0.720 gram of diethoxy soya-amine and 2 milliliters of dichloroethane. The reaction proceeded rapidly to completion, and the deep red solution of the complex displayed IR absorbance at 1410 mμ.

Example 10

Manganous tallate, 1.0 gram was triturated with 2 grams of dimethylethanolamine in 5 milliliters of neutral oil warmed to 30° C. The reaction was completed within 5 minutes and the red manganous-amine coordination complex, in solution in the neutral oil, exhibited IR absorbance at 1410 mμ.

Example 11

Manganous tallate, 1.0 gram was triturated with 3 grams Primeen 81 R (Rohm & Haas, a mixture of tertiary aliphatic primary amines in the C_{12}–C_{14} range) at 30° C. in the presence of 5 grams of neutral oil. The reaction proceeded to completion within 5 minutes and resulted in a deep red-brown solution of the manganous-amine coordination complex in the neutral oil. The solution showed absorbance in the IR at 1410 mμ.

Example 12

Anhydrous manganese chloride, 0.126 gram, was triturated with 0.178 gram of dimethylethanolamine. To the trituration was added 5 milliliters of isopropanol and the resultant mixture was heated, in a flask equipped with a condenser, to 40° C. The flask was maintained at this temperature for 10 minutes until the reaction was complete. The manganous-amine complex in isopropanol was then treated with 10 milliliters of water and a precipitate of the manganous-amine complex came down as a fluffy red-brown powder. This powder, when dried, was redissolved in 3 milliliters neutral oil to which had been added 0.050 gram of dimethylethanolamine. The resultant solution was deep red in color and when it was diluted with 10 volumes of neutral oil exhibited a greenish color by

transmitted light. Diluted solutions of the powder in neutral oil exhibited absorbance in the infrared at 1410 mμ.

Example 13

One pound of manganese tallate (6% Mn) was mixed with half pound of dimethylethanolamine, 1 pound of cresylic acid, and 1 pound of isopropanol. The mixture was then heated to 80–100° F., and the temperature maintained within this range until solution was complete and the colored complex was formed (15 minutes). To this solution containing the manganous-amine complex was added sufficient fuel oil to make 1 gallon of concentrate.

Example 14

One pound of manganous tallate solution (6% Mn by weight) was mixed with half pound of Primeen 81 R., 1 pound of cresylic acid, 1 pound of isopropanol and made up to 5 gallons with neutral oil. The mixture was heated in the range 80–100° F. for 30 minutes by which time the reaction, forming the colored manganous-amine coordination complex, had proceeded to completion. The final red-brown concentrate of the complex exhibited absorbance at 1410 mμ.

Example 15

Five gallons of the concentrate, prepared according to Example 14, was added to 5,000 gallons of No. 6 oil containing 1.95% of sulfur, yielding a treated fuel oil containing 8 parts per million by weight of manganese as the manganous-amine complex. An Economic Fire Tube boiler, equipped with a Ray oil burner, size 7, was used to burn the treated fuel. Prior to this fuel treatment, the SO_2 reading of the stack gases was greater than 150 parts per million by volume determined by the Bachrach SO_2 gas analyzer. Testing after 5,000 gallons of the treated fuel had been consumed, showed the SO_2 content of the stack gases was reduced below 40 parts per million.

Example 16

Anhydrous manganese acetate is slowly added to warm N,N[1]-dimethyl-ethanolamine and mixed until all the acetate is brought into solution in the slight excess of the amine (mole ratio 1:2.6). To this solution is added 60% by weight of an ethoxylated soya-amine (ISO2 Alcolac Chemical Company). This buffered solution is diluted with 24 volumes of neutral oil. This dilution when added in a proportion of 1 part in 2,000 of fuel provides 1.4 parts by weight of manganese, as the complex, per million parts of fuel.

Example 17

No. 6 fuel oil, containing 2.5% sulfur, was treated with the concentrate according to Example 14 in proportions to yield 1.5 parts per million by weight of manganese as the manganous-amine complex. The treated fuel was burned in 300 horsepower Bigelow Water Tube boiler equipment having 35 gallons per hour Petro burners. Untreated fuel oil caused SO_2 concentrations in the effluent stack gases in excess of 150 parts per million. After 30 days feed with treated fuel oil, the level of SO_2 in the stack gases was below 75 parts per million.

Example 18

In a H. B. Smith, low pressure, No. 44 sectional boiler operating on a No. 4 oil containing 1% sulfur, the stack gas Bachrach reading of SO_2 was in excess of 150 parts per million. After four days of the burning of the same fuel oil treated with the additive of Example 14 in an amount sufficient to give a manganese concentration, as the manganese-amine complex, of 6 parts per million by weight of the oil, the SO_2 content of the effluent gases dropped to 40 parts per million.

Example 19

A high pressure, 125 pound Bigelow Fire Tube boiler was burning No. 6 oil with a 3% sulfur content, at the rate of 70 gallons per hour in a rotary-cup burner. The composition of Example 13 was introduced into the fuel oil in a concentration of 10 parts per million by weight of manganese as the manganous-amine complex. The SO_2 concentration of the stack gases dropped from 1800 parts per million to 40 parts per million after 10 days of combustion with the treated fuel.

Example 20

The concentrate of Example 13 was sprayed onto coal being fed into Dillon Fire Tube boilers bed by automatic stokers. The coal was sprayed at the stoker intake with amounts of the concentrate of Example 13 to provide about 12–15 parts per million by weight of manganese as the manganous-amine complex. Table I below summarizes readings made just prior to the use of the treated coal and 6 hours after initiation of the use of the treated coal.

TABLE I

	No additive		With additive	
	Banked fire	High fire	Banked fire	High fire
Percent CO_2	0	4	4	13½
Net stack temp. (° F.)	200	550	200	450
Bachrach smoke	8	10	4	4
Ringleman smoke	4	4	0	0
P.p.m. SO_2	40	50	20	25
Combustion efficiency, percent	[1] 59	[1] 59	80½	83½

[1] Below.

It will be noted from Table I that the combustion efficiency in the boilers was greatly improved. Comparable improved combustion efficiency was also noted in the tests set forth in Examples 15–18. It was also noted during these tests that the smoke was lighter and contained less solids.

Ashes recovered from the combustion tests in industrial installations as set forth in Examples 15–19 revealed that the ashes contained vanadium salts at the vanadous Vn^{+3} stage of oxidation instead of the Vn^{+5} form usually found in the ashes of fossil fuels. The Vn^{+3} salts were primarily sulfur salts with $Vn_2(SO_4)_3$ predominating and some Vn_2O_3 was also present. Recovery of vanadium from such easily soluble vanadium salts greatly enhances the industrial value of the ashes recovered from industrial installations burning fuel compositions according to this invention. Depending on the demand for vanadium, often the increased value of the ashes may pay for the treatment of the fuel with the manganous-amine complexes of this invention.

Example 21

A late model demonstration automobile having less than 15,000 miles on the odometer was used for the test. Using a leaded gas for high compression engines for control and with the manganous-amine complex of Example 14 added in a concentration (1 oz. to 10 gal.) to give 2 parts per million manganese as the complex in the fuel. The following data was recorded after running the automobile for 350 miles (Test A) and 1,000 miles (Test B) on the fuel of this invention.

	Control	Test A	Test B
Percent carbon monoxide:			
Idle	6	----------	
2,000 r.p.m.	7	----------	
15 m.p.h.	3	2	2
30	3	0.5	0.5
40	2	0.5	0.5
50	2.5	1.0	1.0
60	2	0.5	0.5
Smoke (Ringleman):			
Idle	2	----------	
2,000 r.p.m.	6.5	----------	
15	3	1	1
30	2	1	1
40	2	1	1
50	2	1	1
60	2	1	1

Compression readings on the cylinders before and after the test showed a 7% improvement after use of the additive.

Example 22

A Condec 15 HP diesel test engine (diesel-generator) was used. Measurements were made of the sulfur oxides, nitrogen oxides and unburnt hydrocarbons when the engine was operated with a fuel containing 0.18% sulfur (control). The manganous-amine complex of Example 14 was added to this fuel at concentration levels of 2 p.p.m. (Test A), and 10 p.p.m. (Test B) of manganese.

TEST B.—P.P.M. OF MANGANESE

	Control	A	B
CO_2	6.8	7.3	7.8
Unburnt hydrocarbons	102	56	79
SO_2	7.9	17.7	14.3
SO_3	15.4	1.4	1.4
SO_2/SO_3	0.5	12.6	10.2
Nitrogen oxides	1,340	1,120	1,133

Representative manganese amines complexes have been evaluated in single-cylinder test engines as both supplementary and primary antiknock agents in a broad range of commercial fuels. Generally, it has been found that the complexes are satisfactory primary antiknock agents, but in addition, they show excellent supplementary antiknock qualities. In a concentration range of less than 100 parts per million of manganese as the complex, they improve performance of fuels sufficiently to raise commercial "regular" gasoline to "high-test" gasoline quality ratings.

In contrast to usual antiknock materials such as tetraethylead the manganese amine complexes of this invention appear to be completely insensitive to sulfur present as a fuel contaminant. Sulfur is a notable antiknock antagonist for lead-containing antiknock additives. An added feature noted in the testing of the manganese content of this invention is improved combustion. When using test engines with internal surface deposits to check for surface ignition caused by such deposits, it was noted that within a short time surface ignition decreased and disappeared. Upon examination of dismantled engines, it was revealed that the surface deposits were naturally decreased to a point where they no longer initiated surface ignition. After prolonged use it was noted that the internal surface presented a shiny metallic appearance in contrast to the initial heavy coated and contaminated deposits.

Example 23

Fuel containing the concentrate of Example 16 adjusted to 1.0 part per million of manganese was used in furnaces for the melting of glass. Economic review after 4 months of use of the additive showed 5% fuel cost reduction (including the cost of additive) 12% reduction in pot-upkeep and a reduction in acid-smut and visible smoke to below the limits of the Bachrach instruments. Before use of the treated fuel, Bachrach smoke readings ranged between 6 and 10.

Example 24

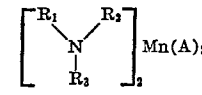
A brick factory in Holland was using No. 6 fuel oil in kiln-firing operations at 1200° C. Variations in the specific gravity of this oil caused uneven feeding rates and uneven heating which resulted in a high product rejection rate due to blistering. In addition, the high sulfur content of the kiln gases also caused rejection of bricks due to sodium silico sulfate embrittlement. The smoke from the brick kiln was in excess of Bachrach 10. Complaints about the smoke pollution problem had led to the use of Barium additives which whitened the smoke but adversely affected the brick structure.

After 2 months of use of the additive of this invention according to Eample 16 in the No. 6 oil in a concentration of 1.5 parts per million of manganese as the complex, a 5% rise in fuel efficiency was noted and the brick rejection rate was reduced 50%. These advantages were attributed to more complete and more uniform combustion and reduced sulfate embrittlement. The smoke pollution problem was abated below Bachrach 1.0, without use of barium and the abatement improved relations between the plant and the community.

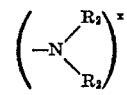
With respect to the various embodiments of this invention set forth in the examples and in the text of the specification, it is to be understood that each embodiment is a preferred one since it had its own advantages for the specific purpose for which it was intended. Further where specific compounds were utilized in certain apparatus, it is understood that the invention is not restricted to such specific compounds in the specific locale. All the useful equivalents of such compounds in such locales or apparatus are deemed suitable for the purpose of this invention and are intended or included thereby.

I claim:

1. A manganous-amine complex having the formula



where A is an anion chosen from the group of manganous salt-forming anions consisting of acetate, chloride, phosphate and fatty acid carboxylate anions; where R_1 is chosen from the group consisting of saturated and unsaturated, substituted and unsubstituted aliphatic radicals having 1 to 22 carbon atoms and radicals of the formula $—(CH_2—CH_2O)_xH$ where x is an integer from 1 to 5; where R_2 is chosen from the group consisting of hydrogen, saturated and unsaturated, substituted and unsubstituted aliphatic radicals containing from 1 to 22 carbon atoms inclusive, and $—(CH_2CH_2O)_XH$ where x is an integer having a value of from 1 to 5; where R_3 is chosen from the group consisting of hydrogen, saturated and unsaturated, substituted and unsubstituted aliphatic radicals containing from 1 to 22 carbon atoms inclusive, $—(CH_2CH_2O)_XH$, where x is an integer having a value of from 1 to 5, and



2. The complex according to claim 1 wherein the manganousamine complex is the colored product formed by the reaction of a manganous salt with an aliphatic amine.

3. The complex according to claim 2 wherein the amine is a primary amine.

4. The complex according to claim 2 wherein the amine is a secondary amine.

5. The complex according to claim 2 wherein the amine is a polyamine.

6. The complex according to claim 2 wherein the amine is dimethylethanolamine.

7. The complex according to claim 2 wherein the amine is N,N-diethoxy soya-amine.

8. The complex according to claim 2 wherein the amine is a branched-chain aliphatic primary amine having 12 to 14 carbon atoms in the aliphatic moiety.

9. The complex according to claim 2 wherein the manganous salt is a manganous carboxylate.

10. The complex according to claim 9 wherein the manganous carboxylate is manganous acetate.

11. The complex according to claim 9 wherein the manganous carboxylate is manganous octoate.

12. The complex according to claim 2 wherein the manganous salt is manganous chloride.

13. A fuel composition for reducing the noxious gas content of exhaust gases which comprises a fuel and an effective amount of the manganous-amine coordination complex of claim 1 dispersed through the fuel.

14. The fuel composition according to claim 13 wherein the fuel is a liquid fuel for internal and external combustion engines.

15. The composition according to claim 13 wherein the fuel is coal.

16. A fuel composition according to claim 13 wherein the manganous-amine complex is the colored product of the reaction of manganous tallate with dimethylethanolamine.

17. A fuel composition according to claim 13 wherein the manganous-amine complex is the colored product of the reaction of manganous tallate with an N,N-diethoxy soya-amine.

18. The fuel composition according to claim 13 whrein the manganous-amine complex is the colored product of the reaction of manganous acetate with an aliphatic primary amine having 12 to 14 carbon atoms in the aliphatic moiety.

19. The fuel composition according to claim 13 wherein the manganous-amine complex is the colored product of the reaction of manganous acetate with dimethylethanolamine.

20. The fuel composition according to claim 13 wherein the manganous-amine complex is the colored product of the reaction of manganous octoate with N,N,diethoxy soya-amine.

21. The fuel composition according to claim 13 wherein the manganous-amine complex is the colored product of the reaction of manganous acetate with a tertiary aliphatic primary amine having 12 to 14 carbon atoms in the aliphatic moiety.

22. The fuel additive comprising at least one manganous-amine complex according to claim 1 dissolved in a fuel-dispersible medium.

23. The fuel additive according to claim 22 wherein said medium is a long chain aliphatic amine.

24. An improved liquid fuel yielding reduced quantities of noxious combustion products consisting essentially of a homogeneous mixture of the fuel and an amount sufficient to provide at least 1 part per million, by weight, of manganese, combined as the complex, of the manganous amine complex as defined according to claim 1.

25. The fuel according to claim 24 wherein the combustible material is a liquid fuel for internal or external combustion.

26. The fuel according to claim 25 wherein the combustible material is gasoline.

27. The fuel according to claim 26 wherein the combustible material is Diesel oil.

28. A fuel composition according to claim 13 wherein the fuel is an oil.

29. The fuel composition according to claim 13 wherein the manganous-amine coordination complex is the colored product of the reaction of manganous tallate with a tertiary aliphatic primary amine having 12 to 14 carbon atoms in the aliphatic moiety.

30. The fuel composition according to claim 13 wherein the manganous-amine coordination complex is the colored reaction product of manganous chloride with dimethylethanolamine.

31. The fuel composition according to claim 13 wherein the manganous-amine coordination complex is the colored reaction product of manganous chloride with N,N-diethoxy soya-amine.

32. The fuel composition according to claim 13 wherein the manganous-amine coordination complex is the colored reaction product of manganous chloride with a tertiary aliphatic primary amine having 12 to 14 carbon atoms in the aliphatic moiety.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,443,916 Dated May 13, 1969

Inventor(s) Andrew T. Rolfe

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 48, that portion of the formula reading

(CH_2CH_2) should read (CH_2CH_2O)

Column 4, line 33, delete "of higher". Column 4, line 35, "monoethenolamine" should read --monoethanolamine--. Column 4, line 37, "diethenol, laurylamine" should read --diethanol laurylamine-- and "diethenolamine" should read --diethanolamine--. Column 4, line 38, "ylamine, diethylamine, triethenolamine, propylamine," should read --amine, ethylenediamine, dodecylamine, octadecylamine,--. Column 4, line 73, "amine" should read --amines--. Column 5, line 59, "leveds" should read --levels--. Column 5, line 69, "andhydrocarbon" should read --and hydrocarbon--. Column 7, line 65, after "formed" insert --which--. Column 11, line 70, "Eample" should read --Example--. Column 12, line 40, outside the second bracket of the formula, "x" should be cancelled. Column 13, line 9, "whrein" should read --wherein--.

SIGNED AND
SEALED
MAR 24 1970

(SEAL)
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