

[54] COAL COMBUSTION PROCESS AND COMPOSITION

3,330,844 7/1967 Kozikowski et al. 44/68 X
3,348,932 10/1967 Kukin 44/4

[75] Inventor: Robert V. Kerley, Ortonville, Mich.

Primary Examiner—Carl F. Dees

[73] Assignee: Ethyl Corporation, Richmond, Va.

Attorney, Agent, or Firm—Donald L. Johnson; Robert A. Linn

[22] Filed: Nov. 23, 1971

[21] Appl. No.: 201,301

Related U.S. Application Data

[63] Continuation of Ser. No. 878,258, Nov. 19, 1969, abandoned, which is a continuation of Ser. No. 723,945, April 24, 1968, abandoned, which is a continuation of Ser. No. 601,558, Dec. 14, 1966, abandoned.

[52] U.S. Cl. 44/4

[51] Int. Cl.² C10L 9/00; C10L 10/00

[58] Field of Search 44/4, 7.5, 68; 110/1 H, 110/1 M, 1 J

References Cited

UNITED STATES PATENTS

902,734 11/1908 Jacobs 44/4

[57] ABSTRACT

A method of reducing the smoke and sulfur trioxide produced when burning coal by introducing a small quantity of a metal cyclopentadienyl compound into the combustion chamber with the coal; a coal composition containing small amounts of the aforesaid metal cyclopentadienyl compounds. The cyclopentadienyl compounds may be introduced into the combustion chamber by any practical means such as, for example, by impregnating the coal with the said cyclomatic compound or by introducing the cyclomatic compound into the combustion chamber separately from the coal. Preferred metal cyclopentadienyl compounds are ferrocene, alkyl ferrocenes, and (methylcyclopentadienyl)manganese tricarbonyl.

10 Claims, No Drawings

1

COAL COMBUSTION PROCESS AND COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of copending application Ser. No. 878,258, filed Nov. 19, 1969 now abandoned, which in turn is a continuation of application Ser. No. 723,945, filed Apr. 24, 1968, now abandoned, which in turn is a continuation of application Ser. No. 601,558, filed Dec. 14, 1966, now abandoned.

BACKGROUND OF THE INVENTION

The invention is directed to an improved method of burning coal and coal compositions used therein.

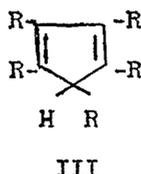
Coal is a common fuel in furnaces used to produce heat and energy. Even though rapid strides have been made in furnace design and construction to improve the combustion of coal, soot, smoke, and irritating gases such as sulfur trioxide formed during the combustion of coal still create a problem. When these combustion products are discharged into the air, they contribute to atmospheric pollution. In addition, the soot generally contributes to decreased efficiency of the burning system by impairing heat transfer and the like.

The introduction of a large excess of oxygen (from air) reduces the soot and smoke formed, but generally increases sulfur trioxide formation. Furthermore, this large excess of air reduces the efficiency of the furnace by carrying away large amounts of heat in the process.

A means of reducing soot, smoke and SO₃ formation in coal burning operations while not reducing the efficiency of the furnace would be an important contribution to the art. The invention hereinafter described provides such a means.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for reducing smoke, soot and sulfur trioxide (SO₃) produced in the combustion of coal. It is a further object of this invention to improve the efficiency and reduce the smoke and SO₃ produced in the combustion of coal by burning the coal with a small amount of a metal cyclopentadienyl compound. Another object of this invention is a coal composition containing a combustion improving quantity of a metal cyclopentadienyl compound.



DESCRIPTION OF THE PREFERRED EMBODIMENTS

An embodiment of this invention is a process for reducing the smoke and SO₃ produced in the combustion of coal, said process comprising burning coal in the presence of a smoke and SO₃ reducing quantity of a metal cyclopentadienyl compound selected from the class consisting of compounds having the Formula (I) AFeA', and (II) AMn(CO)₃, wherein A and A' are independently selected from cyclopentadienyl radicals

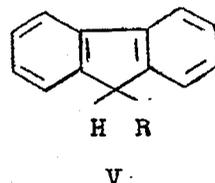
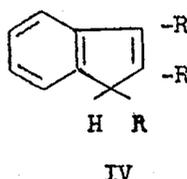
2

having from 5 to about 13 carbon atoms. Another embodiment of this invention is the process described above wherein the quantity of said metal cyclopentadienyl compound present is from about 0.001 to about 5.0 per cent by weight of the coal. Another embodiment of this invention is coal containing a smoke and SO₃ reducing quantity of a cyclopentadienyl compound described above. Preferred embodiments of this invention are compositions of matter or processes described above wherein the cyclopentadienyl compound is dicyclopentadienyl iron (ferrocene), bis(methylcyclopentadienyl)iron, (dimethylferrocene), or (methylcyclopentadienyl) manganese tricarbonyl.

Coal is the general name for the natural rock-like brown to black derivative of forest-like plant usually accumulated in peat beds. The types of coal which are useful in the process of this invention are lignitic coal, represented by brown coal and lignite; bituminous coal represented by sub-bituminous coal; and anthracite coals comprising seminanthracite, anthracite and metaanthracite coals. This coal classification nomenclature is referred to as the rank system. The term rank refers to the stage of carbonification of the coal. This rank system of classifying coal is commonly used in North America. Different names for analogous coal types of the rank system are used in other classification systems and are incorporated by reference. Besides hydrocarbon components, coal also contains sulfur containing materials and compounds.

The organometallic compounds which are used with the coal in the present invention are cyclomatic manganese and cyclomatic iron compounds. Cyclomatic metal organic compounds are those wherein the metal is bonded directly to at least one cyclopentadienyl type hydrocarbon radical. The cyclomatic compounds useful in this invention have the general Formulae I, AFeA', and II, AMn(CO)₃, wherein A and A' are cyclomatic hydrocarbon radicals having from 5 to 13 or more carbon atoms which embodies a group of 5 carbons having the configuration found in cyclopentadiene. The compounds are further characterized in that the cyclomatic hydrocarbon radical A and A' are bonded to the metal by carbon to metal bonds through carbons of the cyclopentadienyl group. Examples of the cyclomatic hydrocarbons from which the cyclopentadienyl metal compounds used in the present invention can be prepared are illustrated by the following structural formulae.

50



wherein R is a substituent selected from the group consisting of hydrogen, alkyl, alkene, cycloalkyl, and aryl radicals.

Specific examples of some of the cyclopentadienes from which useful cyclomatic metal compounds are prepared are cyclopentadiene; methylcyclopentadienes; dimethylcyclopentadienes; trimethylcyclopentadienes; tetramethylcyclopentadienes; pentamethylcyclopentadiene; ethylcyclopentadienes; methyl, ethylcyclopentadienes; n-propylcyclopentadienes; isopropylcyclopentadienes; propenylcyclopentadienes; methyl,

propylcyclopentadienes; n-butylcyclopentadienes; sec-butylcyclopentadienes; tert-butylcyclopentadienes; isobutylcyclopentadienes; amylcyclopentadienes; cyclopentylcyclopentadienes; cyclohexylcyclopentadienes; phenylcyclopentadienes; diphenylcyclopentadienes; pentaphenylcyclopentadienes; indene; fluorene; and the like.

Non-limiting examples of compounds having Formula I in which the cyclomatic radical has the configuration shown in Structures III, IV and V are bis(ethylcyclopentadienyl) irons; bis-[(2-ethylhexyl)cyclopentadienyl]iron; bis(tert-butylcyclopentadienyl) iron; cyclopentadienyl(methylcyclopentadienyl)iron; (1-methyl-2-ethyl-cyclopentadienyl)[(o-tolyl)cyclopentadienyl]iron; (cyclohexylcyclopentadienyl) (phenylcyclopentadienyl)iron; bisfluorenyliron; bisindenyliron; (3-sec-butylindenyl)fluorenyliron; (2-ethylfluorenyl)(2-methylfluorenyl)iron; and the like.

Preferred compounds having Formula I are dicyclopentadienyl iron and bis(methylcyclopentadienyl)iron.

Non-limiting examples of the compounds having Formula II in which the cyclomatic radical has the configuration shown in structures III, IV and V above are cyclopentadienylmanganese tricarbonyl; (butenylcyclopentadienyl)manganese tricarbonyl; (tert-butylcyclopentadienyl)manganese tricarbonyl; (cyclohexylcyclopentadienyl)manganese tricarbonyl; (heptylcyclopentadienyl)manganese tricarbonyl; (pentamethylcyclopentadienyl)manganese tricarbonyl; (1,3-diphenylcyclopentadienyl)manganese tricarbonyl; indenylmanganese tricarbonyl; (1,3-diethylindenyl)manganese tricarbonyl; [3(2-ethylphenyl)indenyl]manganese tricarbonyl; fluorenylmanganese tricarbonyl; (4-propylfluorenyl)manganese tricarbonyl; (4,5,6,7-tetrahydroindenyl)manganese tricarbonyl; (2-ethyl-3-phenyl-4,5,6,7-tetrahydroindenyl)manganese tricarbonyl; (1,4,5,8-tetrahydrofluorenyl)manganese tricarbonyl and the like.

A preferred compound having Formula II is (methylcyclopentadienyl)manganese tricarbonyl.

Mixtures of the cyclomatic metal compounds described above may also be used in the practice of this invention. The mixtures can include only the compounds having Formula I, only compounds having Formula II or combinations of compounds having Formula I and Formula II. Non-limiting examples of useful mixtures are bis(ethylcyclopentadienyl)iron and bis(tert-butylcyclopentadienyl)iron; (cyclohexylcyclopentadienyl)manganese tricarbonyl and bis(methylcyclopentadienyl)iron; (1,3-diethylindenyl)manganese tricarbonyl and cyclopentadienylmanganese tricarbonyl; dicyclopentadienyliron and bis(methylcyclopentadienyl)iron; cyclopentadienyl-(methylcyclopentadienyl)iron and indenylmanganese tricarbonyl; (methylcyclopentadienyl)manganese tricarbonyl; dicyclopentadienyl-iron, and bis(methylcyclopentadienyl)iron; (pentylcyclopentadienyl) manganese tricarbonyl, (phenylcyclopentadienyl)manganese tricarbonyl, (phenylcyclopentadienyl) (tert-butylcyclopentadienyl)iron and the like.

In carrying out the process of this invention, the amount of cyclomatic metal compounds to be employed may vary widely and will depend upon the nature of the coal being burned, the completeness of the combustion desired, the amount of air employed, the type of furnace and other conditions of combustion. In some cases, it may be desirable to use a lesser amount of the cyclomatic metal compound than required to insure complete absence of carbon in the combustion

products. Generally, one part by weight of the cyclomatic metal compound will be used to from 20 to about 200,000 parts by weight of the coal; in other words from 0.0005 per cent to about 5.0 per cent by weight of the cyclopentadienyl compound will be used. Amounts in excess of 5 per cent of the weight of the coal may be used. Such high concentrations, however, may add unnecessarily to the expense.

The means by which the cyclopentadienyl metal compound is introduced along with the coal into the combustion chamber are not critical. Thus, for example, it may be (a) included in the coal, (b) injected into the coal feed, (c) introduced separately into the combustion chamber along with the coal or by any other convenient practicable means. Whatever way it is done, the concentration of the cyclomatic metal compound to coal in the combustion chamber will be within the ranges of specified above.

To illustrate the benefits derived from the present invention, a portion of bituminous coal having a pronounced tendency to smoke is burned in a furnace, with an adequate supply of air. To a second portion of the bituminous coal is added about 0.01 per cent by weight of bis(methylcyclopentadienyl)iron. When this coal composition is burned in the same furnace under the same combustion conditions as the base coal, the quantity of smoke produced is significantly diminished. Similar results are obtained when the coal is powdered, a binder is added along with a small quantity of (methylcyclopentadienyl)manganese tricarbonyl, the composition is pelletized to form a briquette and then the briquette is burned.

The smoke produced in a furnace system which uses powdered coal can also be reduced by using other procedures. In this type of coal furnace, the lump coal is first fed through a grinder; the ground coal then passes directly to a blower system which feeds the combustion chamber. It is self-evident that the smoke can be reduced in this system by using coal compositions of this invention, i.e., coal containing a cyclomatic metal compound to feed the grinder. Another efficient means of introducing the cyclomatic metal compound in this type system is to add the cyclomatic compound to the coal in the grinding operation just prior to combustion. A more efficient method is to introduce the cyclomatic metal compound directly into the ground coal feed as it is blown into the combustion chamber. Another still more efficient process is to add the cyclomatic metal compound into the combustion chamber with the secondary air, that is, the air which is blown into the combustion chamber to improve mixing and to aid combustion in general. This latter process would appear to be most flexible and most economical. It would permit easy and continuous control during the combustion process, thus, permitting adjustment of the metal compound concentration to allow for fluctuations which occur during the combustion cycle. In addition, it would minimize the loss of cyclomatic metal compound during the grinding and feeding steps.

Stoker fed furnaces are also benefited from the process of this invention. Since in this system small lumps (approximately 3/4 inch in the largest dimension) of coal are used, a convenient method of reducing the smoke produced in this furnace is to use stoker coal containing a smoke reducing quantity of cyclopentadienyl metal compound. Preparation of coal containing the cyclopentadienyl metal compound is described below. On the other hand, untreated coal may be used and the metal cyclopentadienyl compound can be metered into this coal at a point between the stoker bin and the

combustion chamber. This latter point could conveniently be in the screw carrying the coal from the bin to the combustion chamber. The cyclopentadienyl compound can be metered in as a powder, as a liquid, as a vapor, as an aqueous slurry or in any other convenient form. As an example of still another method of adding the cyclopentadienyl compound to the combustion chamber, in stoker systems, the metal cyclopentadienyl compound may be introduced directly into the combustion chamber by means of an air feed similar to the secondary air source used in ground coal fired furnaces.

Thus, there are different furnace systems and various means of introducing the cyclomatic metal compound with the coal into the combustion chamber of the furnace. In every case, however, the smoke produced in a coal fired furnace system is noticeably reduced when the coal is burned in the presence of the cyclomatic metal compound.

Besides reducing the amount of smoke and soot produced, it is noted that use of the process of this invention may also diminish the quantity of sulfur trioxide in the coal combustion product. Since sulfur trioxide in the air is recognized as a mucous membrane irritant, the process of this invention would help in air pollution control.

Coal compositions containing a small quantity of the metal cyclopentadienyl compounds having Formula I and II are also an embodiment of this invention. The quantity of metal cyclopentadienyl compounds in the coal compositions corresponds to the range of concentrations described above.

These coal compositions may be prepared by any convenient means. Thus, for example, the metal cyclopentadienyl compound may be applied to the surface of the coal by using an aqueous dispersion of the metal compound and the like. The coal may be coated with a combustible film-forming material containing the proper amount of the cyclopentadienyl metal compound. A more convenient method of preparing the coal compositions of this invention is by physically incorporating the cyclopentadienyl metal compound into the coal as in briquetting. This latter method involves pelletizing powdered coal, a binder and a small quantity of a cyclopentadienyl compound. The briquettes containing the metal cyclopentadienyl compound offer a universally useful form of the composi-

tions of this invention. These briquettes can be used as fuel in any coal burning device from the simple hand-fired domestic stove through the most complex, commercial, ground-coal fired furnace.

The benefits obtained from using a coal composition of the present invention were demonstrated in an evaluation carried out in a commercial coal-fired boiler operation. The evaluation utilized two boilers in a commercial heating plant; each boiler was coal fired and stoker fed. Each boiler was capable of generating 250 psi steam at the rate of 128,000 pounds per hour. Both boilers were operated concurrently and under approximately the same heating loads during the test program. One boiler was operated using untreated stoker coal while the second boiler was operated with stoker coal treated with commercial (methylcyclopentadienyl)manganese tricarbonyl.

The coal was treated with the (methylcyclopentadienyl) manganese tricarbonyl by uniformly spraying the coal after it was loaded into the coal hopper used to feed said second boiler. The commercial (methylcyclopentadienyl)manganese tricarbonyl was sprayed on the coal as a distillate fuel solution. This distillate fuel solution contained about 0.14 pounds of (methylcyclopentadienyl) manganese tricarbonyl per gallon of fuel. The coal was treated at the rate of about 0.5 gallons of this distillate fuel solution per about 1.8 tons of coal. Thus, the treated coal contained about 20.7 grams of (methylcyclopentadienyl)manganese tricarbonyl per ton of coal.

The two boilers were operated under these conditions for a number of consecutive weeks. Visual observations of the smoke level from each boiler stack were made regularly during this period. The flue gases from each of the boilers were sampled regularly and the sulfur trioxide (SO₃) and carbon dioxide (CO₂) content of these gases was determined by routine chemical analysis. The carbon dioxide content in the flue gas is an indication of the efficiency of the combustion system. The higher the CO₂ content, the more efficient is the combustion.

Following is a tabulation of the data obtained in this evaluation. Boiler No. 1 utilized untreated coal; boiler No. 2 utilized coal treated with commercial (methylcyclopentadienyl) manganese tricarbonyl as described above. All concentrations and percentages in these tables are by weight unless otherwise noted.

TABLE 1

Sample Date ⁽¹⁾	SO ₃ and CO ₂ in Flue Gases			
	(A)		(B)	
	Boiler No. 1 Untreated Coal SO ₃ (ppm)	Boiler No. 2 Treated Coal SO ₃ (ppm)	Boiler No. 1 Untreated Coal CO ₂ (%) ⁽²⁾	Boiler No. 2 Treated Coal CO ₂ (%) ⁽²⁾
1st Month				
16	20.8	5.5	9.25	10
19	21.2	18.0	11	11.5
23	8.5	5.0	10.5	10.5
26	11.0	8.0	10.5	11.0
30	48.0	37.5	10	11
2nd Month				
2	44.5	26.5	10	9.75
6	19.5	13.0	10.75	10.5
9	24.5	—	—	—
13	29.5	11.0	8	8.25
16	23.5	24.0	8.25	9
20	12.5	10.5	7.75	8.75
24	17.0	12.0	6	6
27	14.5	12.0	5.5	5.5
30	10.5	13.0	9.5	10.5
3rd Month				
4	9.7	6.7	12	12.25
11	13.2	16.0	10.5	11.5
14	22.0	10.0	10	11
21	50.0	27.0	8.25	10.25

TABLE 1-continued

Sample Date ⁽¹⁾	SO ₃ and CO ₂ in Flue Gases			
	(A)		(B)	
	Boiler No. 1 Untreated Coal SO ₃ (ppm)	Boiler No. 2 Treated Coal SO ₃ (ppm)	Boiler No. 1 Untreated Coal CO ₂ (%) ⁽²⁾	Boiler No. 2 Treated Coal CO ₂ (%) ⁽²⁾
26	24.0	16.0	8.25	11.5
Average	22.3	15.1	9.3	10.0

⁽¹⁾Number indicates day of the month.

⁽²⁾Volume per cent.

Table 2

Month and Date Observed	Visual Smoke (1) Greater Smoke From		
	Boiler No. 1 Untreated Coal	Boiler No. 2 Treated Coal	
1st. 5	X		
6	X		
7	X		
8	X		
9	X		
10	X		
11	X		
12	X		
13	X		
14	X		
15	X		
16	X		
17	X		
18	X		
19		equal	
20		equal	
21		equal	
22		equal	
23			X
24	X		
25	X		
26		equal	
27		equal	
28		equal	
29			X
30		equal	
31	X		
2nd. 1	X		
2	X		
3	X		
4	X		
5		equal	
6		equal	
7		equal	
8			
9	X		
10	X		
11	X		
12	X		
13	X		
14	X		
15	X		
16			X
17		equal	
18		equal	
19		equal	
20	X		
21	X		
22	X		
23	X		
2nd. 24		equal	
25	X		
26	X		
27	X		
28	X		
29	X		
30	X		
3rd. 1	X		
2	X		
3	X		
4	X		
5	X		
6	X		
7	X		
8	X		
9		equal	
10		equal	
11		equal	
12		equal	
13	X		

Table 2-continued

Month and Date Observed	Visual Smoke (1) Greater Smoke From		
	Boiler No. 1 Untreated Coal	Boiler No. 2 Treated Coal	
14			X
15	X		
16	X		
17	X		
18	X		
19	X		
20			X
21			X
22			X
23			X
24		equal	
25	X		
26		equal	
27		equal	
28		equal	

(1) The smoke observations were made during high power demand periods.
(2) X indicates from which boiler more smoke was observed.

The data in the two tables above clearly illustrates the benefits obtained from burning coal treated with small amounts of (methylcyclopentadienyl)manganese tricarbonyl. Table 2 shows that the boiler using the treated coal produced less smoke on the average than the boiler using the untreated coal. The data in Table 1 shows that significantly less sulfur trioxide was found in the flue gases from the boiler using the treated fuel as compared to the SO₃ produced in the boiler using untreated fuel. The nineteen day average of the sulfur trioxide content from boiler No. 2 was 15.1 parts per million (ppm); the average SO₃ from boiler No. 1 was 22.3 ppm.

In addition the data in Table 2 shows that the CO₂ level in the flue gases from boiler No. 2 was higher over the same 19 day period than the CO₂ level in flue gases of boiler No. 1. As pointed out above, this indicates that the combustion efficiency in boiler No. 2 was higher than that of boiler No. 1. Thus, the data shows that coal burned in the presence of a small amount of (methylcyclopentadienyl)manganese tricarbonyl produced less smoke, less sulfur trioxide, and improved combustion efficiency.

Similar results are obtained when dicyclopentadienyl iron, bis(methylcyclopentadienyl)iron and the like are used in place of the (methylcyclopentadienyl)manganese tricarbonyl.

Additional data was obtained in a coal-fired commercial boiler demonstrating the effectiveness of the cyclopentadienyl manganese compounds in reducing the sulfur trioxide content of the flue gas. In this operation (methylcyclopentadienyl) manganese tricarbonyl was diluted with a distillate fuel oil; and this mixture was then fed into the combustion chamber simultaneously with a pulverized coal fuel and burned. The (methylcyclopentadienyl)manganese tricarbonyl mixture was fed

at a rate sufficient to provide about 20 grams of (methylcyclopentadienyl)manganese tricarbonyl per ton of coal. Expressed in weight percent manganese on the coal, this is about 0.0005%. The flue gas samples were taken randomly during an extended period of boiler operation at different steam load levels. Steam load is a measure of boiler output and is expressed in 1,000 lbs./hour units.

The data thus obtained is presented in the following Table.

Table 3

SO ₃ Reduction in Flue Gas			
A.) Coal Fuel — No (Methylcyclopentadienyl)Manganese Added	SO ₃ (ppm) at 690 S.L. (1)	SO ₃ (ppm) at 825 S.L.	SO ₃ (ppm) at 920 S.L.
1	43.9	51.3	43.8
2	47.3	41.4	38.1
3	44.1	52.8	42.0
4	50.5	53.0	42.3
5	51.9	43.1	47.8
6	44.3	50.1	39.3
7	49.6	57.4	51.9
8	45.7	45.8	52.4
9	46.7	49.4	46.7
10			47.6
Avg.	47.5	49.4	45.2

B.) Coal Fuel — (Methylcyclopentadienyl)Manganese Introduced Into Combustion Chamber		
Sample	SO ₃ (ppm) at 525 S.L.	SO ₃ (ppm) at 730 S.L.
a	14.5	20.4
b	14.7	17.8
c	14.3	16.6
d	17.5	16.8
e	17.0	17.1
f	16.5	12.7
g		11.0
h		13.2
Avg.	15.7	16.65

(1) S.L. = Steam load in 1,000 lb/hr

As the data clearly illustrates, burning the coal in the presence of a minute amount of (methylcyclopentadienyl) manganese tricarbonyl resulted in a substantial reduction (about 66%) in the SO₃ content of the flue gas.

The data also illustrates another important point. A representative sample of the coal used in firing the boiler was analyzed spectrographically for manganese. This analysis showed that the coal itself contained from 0.01% - 0.1% manganese. As pointed out above, the flue gas sampling was made randomly over an extended period of time. Allowing that the natural manganese content of the coal would vary between 0.01% - 0.1% over this period, there is no indication from the data in Table 3, Part A that substantial changes in the amount of naturally contained manganese in the coal have any effect on the SO₃ content of the flue gas. In other words, even though the manganese naturally present in the coal fluctuated, the SO₃ levels in the flue gas uniformly ran between 40 and 50 parts per million (ppm).

However, on adding only about 0.0005% of manganese as (methylcyclopentadienyl)manganese tricarbonyl to this coal the SO₃ content of the flue gas was dramati-

cally decreased and consistently ranged between only 14 and 18 ppm (Table 3, Part B). This is convincing evidence that it is not manganese itself, but the particular manganese compound namely a cyclopentadienyl manganese tricarbonyl which is required to effect this unexpected and substantial reduction in SO₃ in flue gas from a coal burning combustion system.

For ease of handling and metering, the cyclopentadienyl manganese tricarbonyl additive is preferably used in admixture with suitable diluents. Examples of suitable diluents are the hydrocarbons such as the distillate fuels, hexane, heptane, nonane, dodecane or other alkanes, kerosenes, toluene xylene, benzene and other low molecular weight aromatics and mixtures of such diluents. Concentrations of the cyclopentadienyl compound in these diluents can range upwards from about 0.1% — preferably from 0.1% to 50%. These concentrates are especially useful where the additive is introduced in minute quantities and directly into the combustion chamber.

The improved process for reducing smoke and SO₃ produced in burning coal and coal compositions used therein have been fully described. Claims to this invention follow. It is intended that this invention be limited only within the spirit and scope of the claims.

I claim:

1. A process for reducing the sulfur trioxide produced in the combustion of coal, said process consisting essentially of burning pulverized coal in a combustion chamber in the presence of a combustion improving quantity of (methyl cyclopentadienyl)manganese tricarbonyl, wherein said coal and said (methylcyclopentadienyl) manganese tricarbonyl are simultaneously but separately introduced into said combustion chamber.

2. The process of claim 1 wherein the quantity of said cyclopentadienyl compound present in from 0.0005% to about 0.01% by weight of the coal.

3. The process of claim 1 wherein said cyclopentadienyl compound is contained in a suitable diluent.

4. The process of claim 3 wherein said cyclopentadienyl compound is introduced in the secondary air feed.

5. The process of claim 3 wherein said cyclopentadienyl compound is introduced in the secondary air feed.

6. The process of claim 2 wherein the concentration of (methylcyclopentadienyl)manganese tricarbonyl is about 0.002% by weight of the coal.

7. The process of claim 5 wherein said (methylcyclopentadienyl)manganese tricarbonyl quantity is from about 0.0005% to about 0.01% by weight of the coal.

8. A combustible fuel composition consisting essentially of a dispersion in air of pulverized coal and (methylcyclopentadienyl)manganese tricarbonyl.

9. The composition of claim 8 wherein said dispersion contains from about 0.0005% to about 0.01% by weight of the cyclopentadienyl compound.

10. The composition of claim 9 wherein said dispersion contains about 0.0005% by weight of the cyclopentadienyl compound.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,927,992
DATED : December 23, 1975
INVENTOR(S) : Robert V. Kerley

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

Column 4, line 18 - after "ranges" - delete -- of --

Columns 7 and 8, Table 2 and Table 2-continued - reposition sub-heading "Treated Coal" and place under "Boiler No. 2"

Column 9, line 47 - "0.01°-0.1%" should be -- 0.01-0.1% --

Column 9, line 50 - "0.01°-0.1%" should be -- 0.01-0.1% --

Column 10, line 17 - "0.1° to 50%" should be -- 0.1 to 50% --

Claim 4 (Column 10, line 41) - "3" should be -- 1 --

Signed and Sealed this

Thirteenth Day of July 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks