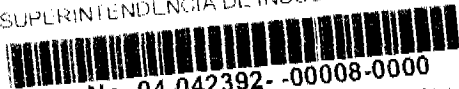


Clarke, M
COLC

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 04-042392- -00008-0000

Fecha: 2010-05-18 15:17:28 Dep. 2020 DIR NUEVAS CR
Tra. 11 PATENTILYII Eve. 379 FASE NACIONAL II
Act 444 RESPUESTA REQUE Folios: 54

P-557

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES
E. S. D.

Re: Expediente No. **04.042.392**

Solicitud de patente a nombre de **CARROLL, ROBERT, W.;
CARROLL, NOEL; CARROLL WILLIAM, F.; CARROLL,
MICHAEL.**

Yo, DILIA RODRIGUEZ D'ALEMAN, identificada como aparece al pie de mi firma, domiciliada en la carrera 11 No. 86-53, piso 6, obrando como apoderada de **CARROLL, ROBERT, W., CARROLL WILLIAM, F., CARROLL, MICHAEL., y CARROLL, NOEL** domiciliados Bradbury, California y Londres, Reino Unido, respectivamente, solicitantes de la patente de la referencia, en respuesta al oficio No. 136 notificado por fijación en lista el 8 de enero de 2010, relacionado con el concepto técnico de fondo No. 4414, cuyo término fue prorrogado mediante escrito radicado el 5 de abril de 2010, me permito manifestar:

1. Con fundamento en la facultad que confiere el artículo 34 de la Decisión 486 al solicitante para modificar la solicitud de patente en cualquier momento del trámite, presento junto con este memorial una nueva descripción y un nuevo capítulo reivindicatorio el cual comprende 1 a 15 reivindicaciones y reemplaza completamente el capítulo anterior.

En cuanto a estas modificaciones, me permito decir que las mismas no amplían de ninguna manera la materia objeto de la presente solicitud y se realizaron con el ánimo de superar las objeciones de claridad, planteadas por el examinador en su concepto técnico.

2. Solicitud Divisional

Con fundamento en la facultad que confiere el artículo 36 de la Decisión 486 al solicitante para dividir en dos o más solicitudes fraccionarias, en cualquier momento del trámite, me permito presentar:

2.1 La patente divisional A titulada: **MÉTODO PARA MEJORAR LA COMBUSTIÓN DE COMBUSTIBLES**, cuya memoria descriptiva y resumen

154
159

Clarke, Modet & Cº

COLOMBIA

corresponden a las mismas de la solicitud CO **04.042.392** como fueron originalmente presentadas y con un nuevo capítulo reivindicatorio que consta de 27 reivindicaciones, que corresponden a las reivindicaciones 1 – 24 y 32 – 34 del capítulo presentado anteriormente

Para este efecto acompaño la siguiente documentación:

- a) Resumen, descripción y capítulos reivindicatorios correspondientes, la memoria descriptiva que explica, ilustra y sustenta las reivindicaciones, la cual se encuentra en el expediente No. **04.042.392**.
- b) Copia del recibo de pago No. 10-18,077, del 8 de enero de 2010, 10-24,887, del 5 de abril de 2010, 10-24,993, del 5 de abril de 2010 y 10-36,670, del 6 de mayo de 2010 con los cuales queda cubierta la tasa de presentación de la nueva solicitud divisional.
- c) Igualmente, solicito a ese despacho tener en cuenta el poder y la cesión que obran en el expediente N° 2004-042.392 de esa superintendencia.

2.2 Teniendo en cuenta lo establecido en el artículo 36 de la Decisión 486, ruego a ese despacho tener en cuenta que las solicitudes divisionales que ahora presento se benefician de la fecha de presentación de prioridad de la solicitud inicial, es decir, el 9 de noviembre de 2001..

3. Claridad de la Solicitud

El examinador insiste en objetar la claridad de las reivindicaciones, argumentando que las mismas no se encuentran debidamente sustentadas por los ejemplos presentes en la descripción. Al respecto, es preciso citar lo establecido por el Artículo 30 de la Decisión 486, el cual dice:

*“Artículo 30.- Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por **la descripción**.”* (Resaltado fuera del texto)

De igual manera, el Artículo 28 de la misma norma es perfectamente claro en cuanto a lo que comprende la descripción:

“Artículo 28.- La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla. La descripción

Clarke, Modet & C^o

COLOMBIA

- a) el sector tecnológico al que se refiere o al cual se aplica la invención;
- b) la tecnología anterior conocida por el solicitante que fuese útil para la comprensión y el examen de la invención, y las referencias a los documentos y publicaciones anteriores relativas a dicha tecnología;
- c) una descripción de la invención en términos que permitan la comprensión del problema técnico y de la solución aportada por la invención, exponiendo las diferencias y eventuales ventajas con respecto a la tecnología anterior;
- d) una reseña sobre los dibujos, cuando los hubiera;
- e) una descripción de la mejor manera conocida por el solicitante para ejecutar o llevar a la práctica la invención, utilizando ejemplos y referencias a los dibujos, de ser éstos pertinentes; y,
- f) una indicación de la manera en que la invención satisface la condición de ser susceptible de aplicación industrial, si ello no fuese evidente de la descripción o de la naturaleza de la invención."

Como se puede apreciar, la descripción no se encuentra limitada únicamente a los ejemplos, sino que comprende muchas otras cosas. Por lo tanto, el requerimiento del examinador de limitar las reivindicaciones a lo divulgado únicamente en los ejemplos va claramente en contra vía de lo establecido por la norma andina que rige la forma y el contenido de una solicitud de patente. La única forma en la que la materia objeto de las reivindicaciones no se encuentra debidamente sustentada por la descripción, es si la misma no se menciona en ninguna parte de dicho capítulo. Como cualquier persona que lea la descripción puede observar que la misma ofrece exactamente la misma lista de catalizadores o mejoradores de combustión que se encuentra en las reivindicaciones, por lo tanto las mismas si se encuentran debidamente sustentadas por la descripción, según lo establecido por la norma andina.

Ahora bien, si lo que el examinador busca es ejemplos funcionales y pruebas comparativas de absolutamente todos las posibles combinaciones de la solicitud, se le recuerda que el solicitante no esta obligado a proporcionar tal información, y así la proporcionara, los ejemplos no son de carácter limitante ya que lo único que determina el alcance real de la invención es el capítulo reivindicatorio, como bien lo ha establecido el Tribunal Andino en múltiples ocasiones.

Por último, se le recuerda al examinador que el solicitante se encuentra amparado por el principio de buena fe establecido en la constitución nacional, por lo tanto todo lo reclamado en la solicitud debe ser tenido por cierto a menos que ese Despacho, como la parte acusadora, proporcione evidencia que demuestre lo contrario. Puesto que el examinador no ofrece ningún tipo de evidencia documental o experimental que demuestre que alguna de las combinaciones propuestas por el solicitante no posee la actividad reclamada, se deriva que todas las combinaciones cumplen con lo establecido por la descripción y deben ser

161
761

Clarke, Modet & C^o

COLOMBIA

propuestas por el solicitante no posee la actividad reclamada, se deriva que todas las combinaciones cumplen con lo establecido por la descripción y deben ser aceptadas por el examinador.

Por otro lado, se ha modificado el capítulo reivindicatorio para limitar el alcance de la invención únicamente a las composiciones, dejando las reivindicaciones relacionadas con el método en la solicitud divisional anexa.

En resumen, me permito decir que gracias a los argumentos anteriormente mencionados, la presente solicitud cumple cabalmente con el requisito de claridad respecto la composición expuesta en el capítulo reivindicatorio. Por lo tanto, solicito comedidamente a ese despacho se sirva reconocer estos requisitos y conceder el privilegio de patente de invención a la solicitud en estudio.

En consecuencia, solicitamos a ese despacho pronunciarse en relación con todos los argumentos presentados en este memorial dando estricta aplicación al principio del debido proceso consagrado en el artículo 29 de la Constitución Nacional. De igual forma, si el examinador considera que subsisten razones para objetar la presente invención ruego expedir otro examen de fondo con los debidos motivos y razones que sustenten su objeción con el fin de que mi mandante tenga la posibilidad de exponer sus argumentos con base en la interpretación de los artículos 45 de la Decisión 486 -el cual otorga la facultad al examinador para emitir los exámenes de fondo-, 35 y 59 del Código Contencioso Administrativo que señala que: *"habiéndose dado oportunidad a los interesados para expresar sus opiniones, y con base en las pruebas e informes disponibles, se tomará la decisión que será motivada al menos en forma sumaria si afecta a particulares"* y *"(..) deberá proferirse la decisión definitiva. Esta se motivará en sus aspectos de hecho y de derecho, y en los de conveniencia si es el caso"*, respectivamente (el subrayado es nuestro).

Señor Superintendente,



DILIA MARÍA RODRÍGUEZ D' ALEMAN
C.C. 41.654/882 de Bogotá.
T.P. 20824 CSJ

REIVINDICACIONES

1. Una composición de combustible líquido, sólido o gaseoso y uno o más catalizadores o mejoradores de combustión en la cual el catalizador o mejorador de combustión está presente en una concentración menor que 1 parte en peso de catalizador o mejorador de combustión por 500 millones de partes de combustible y mayor o igual que 1 parte en peso de catalizador o mejorador de combustión por 6 billones de partes de combustible.

2. La composición de la reivindicación 1 en donde uno o más de los catalizadores o mejoradores de combustión se seleccionan de al menos uno de óxido de rutenio (IV), cloruro de rutenio (III), trihidrato de cloruro de rutenio (III), bromuro de rutenio (III) y sus hidratos, acuopentaclororutenio (III) de amonio, óxido de rutenio (VI) de potasio, óxido de rodio (III), cloruro de rodio (III) y sus hidratos, nitrato de rodio y sus hidratos, cloruro de iridio (III), óxido de iridio (III), óxido de iridio (IV), hidruro de hexacloroiridio (IV) y sus hidratos, amonio de hexacloroiridio (IV) y sus hidratos, tetraóxido de osmio, cloruro de osmio (III), negro de platino, óxido de platino (IV) y sus hidratos, cloruro de platino (II), cloruro de platino (IV), cloruro de polivinilo, hidrato de hidruro de hexacloroplatino (IV), hidruro de hexahidroxoplatino (IV), monohidrato de cloruro de tetraaminoplatino (II), dinitrodiaminoplatino (II), dihidruro de sulfatodinitrilo de platino (II), dinitrato de tetraaminoplatino (II), cloruro de paladio (II), óxido de paladio (II), nitradihidrato de paladio (II), amonio de hexacloropaladio (IV), nitrato de tetraaminopaladio (II), trihidrato de tetracianopaladio (II) de potasio, prrhenato de potasio, cloruro de renio (III), tris(acetilacetanoato) de renio (III), cis-dicloro(2,2'-bipiridin paladio (II), dicloro(1,5-ciclooctadien) platino (II), nitrato de 2-hidroxietanotiolato(2,2',2''-terpiridin) platino (II), tricarbonilcloroiridio (I), dímero de cloro(1,5-ciclooctadien) iridio (I), cloruro de trans-diclorobis(etilendiamin)iridio (III), dímero de octanoato de rodio (III), acetilacetanoato(1,5-ciclooctadien) rodio (I), acetilacetanoato(norbornadien) rodio (I), hidrotatrakis(trifenilfosfin)rodio (I), diacetatobis(trifenilfosfin)paladio (II), Bis(dinecilidenacetona) paladio (O), dicloro [1,2-bis(difenilfosfino)etan] paladio (II), trifluoroacetato de paladio (II), acetatohidridotris(trisfenilfosfin)rutenio (II), Bis(bencen)diclorodi-mu-clrodirutenio (II), Tris(2,2'-bipiridin)rutenio (O), carbonildihidrotris(trifenilfosfin)rutenio (II), Bis(ciclopentadienil)rutenio (II) "Ruthenocene", dihidridotetrakis(trifenilfosfin)rutenio (II), hdxfluoroacetil acetanoato de rutenio (II), nitrato de amonio, dicloroetilendiaminplatino (II), Bis(acetilacetanoato)platino (II), Diclorobis(trifenilfosfin)plartino (II), tetrakis(trifenilfosfin)platino (O), Bis(acetilacetanoato)paladio (II), dicloro(cicloocta-1,5-dien)paladio (II), dímero de cloro(pi-alil)paladio (II), trímico de acetato de paladio (II), tris(acetilacetanoato)rutenio (III), hidrocarboniltris(trifenilfosfin)rodio (I), acetilacetanoatodicarbonilrodio (I), tris(acetilacetanoato)rodio (III), bromotris(trifenilfosfin)rodio (I), dímero de acetato de rodio (II), tris(acetilacetanoato)iridio (III),

Dodecacarboniltrisoscio (O).

3. La composición de la reivindicación 1 en donde uno o más de los catalizadores o mejoradores de combustión se seleccionan de al menos uno de cloruro de paladio (II) o el bromuro, yoduro, hidrato de nitrato, óxido, hidrato de sulfato e hidróxido; tris(dibencilidenacetona)dipaladio (O); dicloro(1,1-bisdifenilfosfino)ferrocenpaladio (II); dímero de cloruro de alilpaladio (II); trans-diclorobis(acetonitrilo)paladio (II); trans -diclorobis(benzonitril)paladio (II); trans-diclorobis(trifenilfosfin)paladio (II); trans-acetato(trifenilfosfin)paladio (II); dicloro(norbornadien)paladio (II); 2,4-pentandionato de paladio (II); cloruro de platino (II); cloruro de platino (IV), o bromuro, o yoduro o sales de sulfato; hidrato de óxido de platino (IV) (Catalizador Adamasi); 2,4-pentandionato de platino (II); dibromo(1,5-ciclooctadien)platino (II); diyodo(1,5-ciclooctadien)platino (II); difenil(1,5-ciclooctadien)platino (II); diclorobis(acetonitril)platino (II); diclorobis(benzonitril)platino (II); dicloro(norbornadien)platino (II); dihidrógeno de hexacloroplatino (IV); hidrato de cloruro de rodio (III); yoduro de rodio (III), u óxido, o sales de sulfato o bromuro; 2,4-pentadieno de rodio (III); dicarbonil 2,4-pentadieno de rodio (I); clorotris(trifenilfosfin)rodio (I); bromocarbonilbis(trifenilfosfin)rodio (I); clorocarbonilbis(trifenilfosfin)rodio (I); dímero de cloro(norbornandien)rodio (I); tetrafluoroborato de bis(1,5-ciclooctadien)rodio (I); hidrato de cloruro de rutenio (III) o las sales de óxido, bromuro, yoduro y amino; diclorotris(trifenilfosfine)rutenio (II); dímero de diclorotricarbonilrutenio (II); 2,4-pentandionato de rutenio (III); oligómero de dicloro(1,5-ciclooctadien)rutenio (III); dicarbonilbis(trifenilfosfin)rutenio (II); tri-rutenio (0) dodecacarbonilo; nitrosilnitrato de rutenio; hidrato de cloruro de iridio (IV), sales de cloruro, óxido, hidróxido, bromuro, sulfato o yoduro de iridio (III); 2,4-pentandionato de iridio (III); 2,4-pentandionato de dicarboniliridio (I); clorocarbonilbis(trifenilfosfin)iridio (I); hidridocarboniltris(trifenilfosfin)iridio (I); tetrafluoroborato de bis(1,5-ciclooctadien)iridio (I); óxido de osmio (VIII).

4. La composición de la reivindicación 1 en donde uno o más de los catalizadores o mejoradores de combustión se seleccionan de al menos uno de sales de fluoruro, cloruro, bromuro, sulfato, nitrato e hidratos en forma soluble de los siguientes metales: lantano, cerio, praseodimio, neodimio, prometio, samario, europio, gadolinio, terbio, disprosio, holmio, erbio, tulio, yterbio, lutecio.

5. La composición de la reivindicación 1 en donde uno o más de los catalizadores o mejoradores de combustión se seleccionan de al menos uno de sales de fluoruro, cloruro, bromuro, sulfato, nitrato e hidratos en forma soluble de los siguientes metales: cobalto, níquel, manganeso, hierro, cobre, molibdeno, vanadio, circonio, berilio, cromo, aluminio, torio, cadmio, estaño, cesio, potasio, sodio, tantalio, titanio, carbono, litio.

6. La composición de la reivindicación 1, en la cual el catalizador o mejorador de combustión está presente en una concentración menor que 1 parte en peso de

catalizador o mejorador de combustión por 500 millones de partes de combustible y mayor que 1 parte en peso de catalizador o mejorador de combustión por 3 billones de partes de combustible.

7. La composición de la reivindicación 1, en la cual el catalizador o mejorador de combustión está presente en una concentración menor que 1 parte en peso de catalizador o mejorador de combustión por mil millones de partes de combustible y mayor que 1 parte en peso de catalizador o mejorador de combustión por 3 billones de partes de combustible.

8. La composición de la reivindicación 1, en la cual el catalizador o mejorador de combustión está presente en una concentración de entre 1 parte en peso de catalizador o mejorador de combustión por 100 mil millones de partes de combustible y 1 parte en peso de catalizador o mejorador de combustión por 6 trillones de partes de combustible.

9. Una mezcla de al menos un catalizador o mejorador de combustión seleccionado de aquellos definidos arriba y uno de agua y un líquido hidrofílico/oleofílico, en donde el catalizador o mejorador de combustión esta presente en la mezcla en una concentración de entre 1 parte en peso por 12 billones de partes de la mezcla y 1 parte en peso por 100 millones de partes de la mezcla.

10. La mezcla de la reivindicación 9, en donde el al menos un catalizador o mejorador de combustión es como se define en las reivindicaciones 2 a 5.

11. La mezcla de cualquiera de las reivindicaciones 9 o 10, en donde el líquido hidrofílico/oleofílico es uno o más de alcohol isopropílico, metanol, etanol y MTBE, metiletilcetona, metilisobutilcetona y metanol

12. La composición de la reivindicación 1, la cual comprende además un solvente seleccionado de alcohol isopropílico, metanol, etanol y MTBE, metiletilcetona, metilisobutilcetona y metanol o mezclas de los mismos.

13. La composición de la reivindicación 1, la cual comprende además un compuesto hidrofílico/oleofílico seleccionado de alcohol isopropílico, metanol, etanol y MTBE, metiletilcetona, metilisobutilcetona y metanol o mezclas de los mismos.

14. La composición de la reivindicación 1, la cual comprende además un medio compatible con el combustible seleccionado del grupo que comprende alcohol isopropílico, metanol, etanol y MTBE, metiletilcetona, metilisobutilcetona y metanol o mezclas de los mismos.

15. La composición de la reivindicación 1, en la cual el catalizador o mejorador de combustión está presente en una concentración menor que 1 parte en peso de

catalizador o mejorador de combustión por 500 millones de partes de combustible y mayor que 1 parte en peso de catalizador o mejorador de combustión por 6 billones de partes de combustible.

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020
Bogotá, D.C., (30 de Agosto 2010)

Abogado
Dilia Maria Rodríguez D'alemán
(Apoderado)

Solicitante: Carrol Robert, Carrol Noel, Carrol William F, Carrol Michael.

ASUNTO	Radicación	04-42392
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	11671
	Folios	005

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☐

Vía PCT (fase nacional) ☒ Cap. I ☐ Cap. II ☒

No. Sol. Internacional PCT /AU02/01519
Fecha de Presentación Internal. 8 DE Noviembre del 2002

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- 1.1. Descripción: Folios: 31 a 56
- 1.2. Reivindicaciones: Folios 57 a 63 (capítulo reivindicatorio original)
Folios: 143 a 151 (capítulo reivindicatorio modificado)
Folios: 162 a 165 (capítulo reivindicatorio modificado)
- 1.3. Prioridad: 9 de Noviembre del 2001, Gran Bretaña, No. solicitud 0126990.1

El solicitante presentó modificaciones al capítulo reivindicatorio las cuales fueron aceptadas. Sobre el capítulo reivindicatorio modificado se emite el presente concepto.

2. Análisis de la Prioridad

Comparando la materia presentada en el documento presentado como prioridad, por parte del solicitante, con respecto a la materia presentada en la solicitud, se encuentra que coincide por lo que la prioridad es aceptada.

3. Objeto de la invención

- *Título de la solicitud: "Método y composición para mejorar la combustión de los combustibles". De acuerdo a las modificaciones realizadas a la solicitud el título más conveniente es: "Composición para mejorar la combustión de los combustibles".*

El objeto de la presente solicitud de patente de invención consiste en:

Reivindicaciones 1 a 15: Una composición de combustible líquido, sólido o gaseoso y uno o más catalizadores mejoradores de combustión en la cual el catalizador o mejorador de combustión está presente en una concentración menor que 1 parte en peso de combustible y mayor o igual que 1 parte en peso de catalizador o mejorador de combustión por 6 billones de partes de combustible.

El solicitante en el capítulo descriptivo presenta el siguiente objeto de la solicitud: "La presente invención se refiere a la combustión mejorada de los combustibles y en particular los combustibles a base de hidrocarburos. Más particularmente, la invención se refiere a un método y composición para mezclar un catalizador o mejorador con combustible para mejorar la combustión en un motor".

- *Clasificación Internacional de Patentes (IPC). C 10 L 1/10*

4. De la solicitud de Patente

4.1. Reivindicaciones (artículo 30 D 486)

En términos de patentes las composiciones se caracterizan por medio de los componentes y las proporciones en las que estos se encuentren, de esta manera en la reivindicación 1 de la solicitud se deberían especificar los compuestos que conforman la composición ya que la reivindicación 1 solamente enuncia el combustible y el catalizador pero se deberían mencionar los compuestos que se consideran como catalizadores.

De acuerdo a lo anterior el capítulo reivindicatorio no cumple con lo establecido en el art. 30 de la Decisión 486 y/o art. 22 Tratado PCT.

5. Determinación del Estado de la Técnica

La fecha que se ha tenido en cuenta para determinar el Estado de la Técnica es la fecha de presentación de la solicitud prioritaria la cual corresponde al 9 de Noviembre del 2001. Teniendo en cuenta la fecha indicada se realizó la búsqueda en el estado de la técnica de documentos relacionados con la solicitud encontrándose los siguientes documentos más relevantes:

Nº	Documento	Título	Fecha de publicación
D1	US 4891050	Gasolina additives and gasolina containing soluble platinum group metal compounds and use in internal combustion engines	2 enero 1990
D2	US 4629472	Method and apparatus for improving combustion, thermal efficiency and reducing emissions by treating fuel	16 Diciembre 1986

6. Análisis de patentabilidad (artículo 14 D486)

6.1. Nivel inventivo (artículo 18 D486)

En la anterioridad D1 se presenta la aplicación de compuestos de platino a los cuales son solubles en combustibles a base de gasolina o en solventes que son utilizados en motores de gasolina. Los compuestos son utilizados en pequeñas cantidades por lo que logra un efecto catalítico para ellos las cantidades se encuentran entre 0.01 a 1.0 partes del metal de platino por un millón de partes de gasolina (ppm). Los solventes utilizados son preferiblemente hidrocarburos oxigenados tales como etanol, tetrahidrofurano y metil butil eter y se encuentran en una proporción de menos del 5% del peso del combustible.

Los compuestos del grupo de platino presentan estados de oxidación +2 y +4 con al menos un sitio de coordinación el cual es ocupado por un grupo funcional que contiene al menos un enlace carbono-carbono insaturado con una configuración de enlace π para grupos de olefinico, acetilénico y aromáticos. Dentro del grupo de metales de platino se encuentran platino, paladio, rodio, rutenio, osmio e iridio especialmente platino en combinación con paladio y/o rodio.

Las composiciones de los aditivos de la invención aumentan la eficiencia de la combustión interna de los motores de gasolina y diesel y disminuyen las emisiones de partículas y gases nocivos tales como monóxido de carbono y monóxido de nitrógeno.

En la anterioridad D2 se esta presentando una lista de los compuestos que son considerados como catalizadores y de los cuales se emplean entre 0,005 a 0,5 ppm en los combustibles para proveer una eficiencia térmica en la combustión, reducir emisiones de gas, suprimir las producción de NOx y SO₃. Dentro de los compuestos listados se encuentran sales de rutenio, rodio, iridio, osmio, platino, paladio.

200769

De acuerdo a la información presentada en las anterioridades es posible establecer que las composiciones en las cuales se encuentra presente un combustible, un catalizador del grupo de metales de platino y solventes hidrofílicos; es posible derivarlas del estado del arte ya que tanto los catalizadores empleados en la composición de la invención como en las anterioridades son los mismos y en las anterioridades también se están empleando en mínimas cantidades obteniendo reducción de emisiones gaseosas y material particulado así como una eficiencia energética en la combustión de los motores a gasolina o diesel.

Por lo tanto, la composición de la solicitud no presenta la suficiente altura inventiva para ser diferenciada de lo revelado en el estado del arte y por ende carece de Nivel Inventivo.

7. Conclusión:

Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	Documento N°	Reivindicaciones afectadas	Requisito que afecta
D1	US 4891050	1 a 15	Nivel Inventivo
D2	US 4629472	1 a 15	Nivel Inventivo

7. Respuesta a los argumentos del solicitante:

La solicitud presenta falta de claridad ya que en la reivindicación 1, considerada como la reivindicación principal en la cual se encuentra contenida toda la invención se enuncia que la composición contiene un catalizador pero no especifica el catalizador al cual se refiere. Por lo tanto, la composición definida en la reivindicación 1 debería contener todos los componentes que conforman tal composición.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

ALIX CARMENZA CESPEDES DE VERGEL
Directora de Nuevas Creaciones (C).

El anterior requerimiento fue notificado por fijación en lista, de fecha 12.0 SET. 2010

CONCEPTO TÉCNICO No. 3151	EXAMINADOR TÉCNICO Código No.202064
-------------------------------------	---

**GASOLINE ADDITIVES AND GASOLINE
CONTAINING SOLUBLE PLATINUM GROUP
METAL COMPOUNDS AND USE IN INTERNAL
COMBUSTION ENGINES**

RELATED APPLICATIONS

This application is a continuation-in-part of commonly assigned co-pending patent application Ser. No. 796,428 filed Nov. 8, 1985, now abandoned which in turn is a continuation-in-part of prior applications Ser. No. 677,954, now abandoned filed on Dec. 4, 1984, and Ser. No. 790,738, filed on Oct. 24, 1985, now abandoned all by Bowers and Sprague, the inventors herein.

TECHNICAL FIELD

The present invention relates to improving the performance of internal combustion gasoline engines, and, more particularly, to the formulation and use of gasoline additives and fuels which burn more efficiently and with reduced noxious emissions.

Background Art

Prior investigations involving the use of platinum group metals in internal combustion gasoline engines have led to the development of the catalytic converter for emissions reduction. Reliance upon costly mechanical equipment, while less than ideal or desirable, has become standard despite the efforts of the prior art to accomplish the same result through less costly combustion improvements in terms of better combustion conditions through engine design and fuel additives. The efforts in engine design have provided significant improvements, but the twin objectives of improved operating efficiency and reduced noxious emissions are difficult to achieve simultaneously.

Experience to date with gasoline additives has been less successful. Lyons and McKone, for example, disclose in U.S. Pat. Nos. 2,086,775 and 2,151,432, adding from 0.001 to 0.085% (i.e., from 10 to 850 parts per million) of an organometallic compound or mixture to a base fuel such as gasoline, benzene, fuel oil, kerosene, or blends to improve various aspects of engine performance. Among the metals disclosed in U.S. Pat. No. 2,086,775 are cobalt, nickel, manganese, iron, copper, uranium, molybdenum, vanadium, zirconium, beryllium, platinum, palladium, chromium, aluminum, thorium and the rare earth metals, such as cerium. Among those disclosed in U.S. Pat. No. 2,151,432 are selenium, antimony, arsenic, bismuth, cadmium, tellurium, thallium, tin, barium, boron, cesium, didymium, lanthanum, potassium, sodium, tantalum, titanium, tungsten and zinc. In both disclosures, the preferred organometallic compounds were beta diketone derivatives and their homologues, such as the metal acetylacetonates, propionylacetonates, formylacetonates, and the like. While such compounds typically provide oxygen-to-metal ratios in the range of 1:1 to 1:10, no essential feature linked to the presence of oxygen is disclosed.

The Lyons and McKone disclosures state that concentrations of from 0.001 to 0.04% (i.e., from 10 to 400 parts per million) are not effective to improve combustion efficiency as introduced, but may become so upon prolonged use as catalytically active deposits are built up in the combustion chamber. The disclosure further states that about 0.01% (i.e., 100 ppm) of the organometallic compound is usually sufficient, once the requisite amount of catalytically active deposits has been built

up, to perpetuate that amount of deposits by replacement of losses therefrom. The compounds disclosed were, therefore, not capable of generating any instantaneous catalytic effect at low concentrations, and to higher concentrations would provide no economic benefit. U.S. Pat. No. 2,460,780 to Lyons and Dempsey, which relates principally to water-soluble catalysts, confirms this at column 1, lines 11-36. Further, no indication was made for preferred oxidation states for the metals disclosed.

Neither of the Lyons and McKone patents disclose the use of oxygenated solvents or point to the importance of high oxygen-to-metal ratios. In Demonstration 15 in U.S. Pat. No. 2,086,775, palladium acetylacetonate was added to a fuel (not specifically identified, but presumably the leaded 65 octane gasoline employed in Demonstration 1) at a level of 0.002% (20 ppm). The weight ratio of oxygen to palladium was not mentioned, although by calculation it is found to be about 1 to 3, and the level of palladium is found to be about 10 ppm. No improvement in combustion was noted until after substantial driving.

The above-noted U.S. Pat. No. 2,460,780 to Lyons and Dempsey relates principally to employing catalysts which are soluble in water or other "internal liquid coolants" such as alcohol, water-soluble glycols or aqueous solutions of these. While catalyst levels based on the weight of metal compounds as low as 0.001% are disclosed, it is stated that for immediate catalytic effect the catalyst compounds for useful effect may be present at a level of at least 1% of the weight of the operating fuel charge. In some Examples, fuel-soluble cobalt, cerium and chromium catalysts are added to the fuel at total catalyst levels of 0.01%. No disclosure is given of fuel-soluble catalysts at levels below 0.01% or with oxygenated solvents. Moreover, where alcohol and glycols are employed with water-soluble catalysts, they are disclosed principally as solubilizing carriers for the catalysts and for their known internal cooling function at high load.

U.S. Pat. No. 4,295,816, Robinson discloses an elaborate delivery system for introducing water-soluble platinum group metal salts through the air intake of internal combustion engines to deliver platinum group metal catalysts to the combustion chamber at a level no greater than 9 mg catalyst per kilogram of fuel. The equipment is, unfortunately, more complicated than would be desired for gasoline automotive operators and the water-soluble salts employed, e.g., hoids, have disadvantages alone or when dissolved.

In German Offenlegungsschrift No. 2,500,683, Brantl discloses that a wide variety of catalytic metals may be added to hydrocarbon fuels to reduce nitrogen monoxide and oxidize carbon monoxide at the moment of combustion in internal combustion engines. The disclosure states that organometallic or Grignard compounds of the metals lithium, sodium, lead, beryllium, magnesium, aluminum, gallium, zinc, cadmium, tellurium, selenium, silicon, boron, germanium, antimony and/or tin can be added to the fuel individually or as a mixture. Similarly, the metal complexes of the metals scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, palladium, osmium, iridium, platinum, silver, gold, gallium, molybdenum, lead and mercury, with different ligands, can be added to the fuel individually or as a mixture. For the platinum group metals osmium, iridium, and

platinum, broad concentrations of from 0.347 to 3.123 grams per liter of fuel are suggested for the various compositions listed in the disclosure, with the range for particularly favorable results being from 0.868 to 1.735 grams per liter of fuel. Considering the cost of these metals and the compositions containing them, there is a negative incentive for employing them at the high levels stated by the disclosure to be effective. Moreover, the tetramethyl platinum compound is not known to exist.

In U.S. Pat. No. 2,402,427, Miller and Lieber disclose the use of certain diesel-fuel-soluble organic or organo-metallic compounds as ignition promoters at concentrations of from 0.02 to 3% (i.e., 200 to 30,000 parts per million). No platinum group metal compounds are identified and no indication is given that the disclosed compounds at the disclosed or lower levels would improve combustion in a gasoline internal combustion engine.

Other work done, in which cylinders of a diesel engine were coated with platinum metal, showed reductions in noxious emissions, but the coating wore off in a number of hours.

DISCLOSURE OF INVENTION

The present invention comprises the application of certain platinum group metal compounds which are directly soluble in gasoline-based fuels, or solvents for use in gasoline engines. The compounds, preferably in combination with a solvent for them which is also miscible in the gasoline, are employed at very small, but catalytically effective levels to provide from about 0.01 to about 1.0 parts of platinum group metal per one million parts of gasoline (ppm). For the purposes of this description, all part per million figures are on a weight to volume basis, i.e., mg/liter, and percentages are given by weight, unless otherwise indicated.

According to one its aspects, the invention provides gasoline additive compositions comprising a solution of a fuel-soluble platinum group metal compound in a solvent miscible in the fuel, the platinum group metal compound being present in an amount sufficient to supply from 0.01 to 1.0 parts per million of the platinum group metal when added to a predetermined amount of fuel.

Preferred solvents are oxygenated hydrocarbons such as ethanol, tetrahydrofuran, and methyl tertiary butyl ether, and will preferably be employed in amounts of less than 5% of the weight of the fuel. The oxygenated solvents will preferably be employed in amounts sufficient to supply oxygen at a weight ratio to the platinum group metal of at least 1000:1.

Among the preferred platinum group metal compounds are platinum group metal coordination compounds comprising a platinum group metal having a +2 or +4 oxidation state with at least one coordination site in the compound being occupied by a functional group containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration. Especially preferred compounds are those of the formula:



wherein X is a cyclooctadienyl ligand; M is a platinum group metal; and R is benzyl, phenyl or nitrobenzyl.

According to another aspect of the invention, gasoline fuel compositions of improved properties are provided, which comprise gasoline and an additive composition dissolved therein, said additive composition com-

prising a fuel-soluble platinum group metal compound in an amount effective to supply from 0.01 to 1.0 parts of the platinum group metal per million parts of fuel.

According to a further aspect of the present invention, there is provided a method of increasing the utilizable energy of gasoline for powering internal combustion engines, comprising admixing with said gasoline an additive composition comprising a fuel-soluble platinum group metal compound in an amount effective to supply from 0.01 to 1.0 parts of the platinum group metal per million parts of fuel.

The additive compositions according to the invention improve operating efficiency of gasoline and diesel internal combustion engines in terms of increased power output per unit of gasoline burned and reduce the emissions of particulates and noxious gases such as carbon monoxide and nitrogen monoxide. The additives provide beneficial results upon immediate use and over long periods of continuous use.

For the purposes of this description, gasoline is defined as a mixture of volatile hydrocarbons for use in a spark-ignited internal combustion engine and having an octane rating [(Research+Motor)/2] of at least 80, typically about 87 to 89 or above, and according to the more preferred aspects of the invention as having less than 1.4 grams per gallon of lead. Most preferably, the gasoline will be "unleaded" and contain no more than 0.05 grams of lead per gallon and no more than 0.1% of sulfur. Gasoline typically has a BTU value of about 19,700 calories per pound.

The gasoline additive compositions of this invention achieve the most reproducible effect in engines operated under lean conditions namely an air/fuel ratio of about 14.7:1 or leaner, so that oxygen is available. Compression ratios in the range of 7:1 to 12:1 are preferred. The additive is believed to improve combustion efficiency by speeding up flame initiation from the spark and increasing subsequent flame speed. It is well known that each cycle in a spark ignition engine varies around a mean optimum pressure pattern with maximum pressure occurring shortly after top-dead-center. This invention is believed to reduce the so-called "cyclic variation" from this optimum and thus increases the power for the same amount of fuel, which improves fuel consumption. This theory is provided to help explain the unexpected results achieved but is not meant to be limiting in any regard.

As indicated above, the preferred platinum group metal compounds are coordination compounds. These compounds, especially those coordinated with certain high molecular weight (preferably above 100 daltons) olefinic functional groups, are stable in the presence of moisture. This is extremely important due to the amounts of water present in gasoline which, for example, can typically contain dissolved water in amounts on the order of 30 ppm and frequently contains higher levels of dispersed and bulk water.

Few, if any, platinum group metal coordination compounds which are directly soluble in gasoline are available commercially. Compounds which are available often contain objectionable functional groups containing halogen and phosphorus and, therefore, are less than preferred for many internal combustion applications. Preferably, the compounds according to the present invention will have no phosphorus or have low levels which are free of significant disadvantages. We have discovered that certain platinum group metal com-

pounds can be prepared which are soluble and stable in gasoline based fuels and actively catalyze the combustion of gasoline in internal combustion engines and reduce noxious emissions when introduced as an integral part of the fuel.

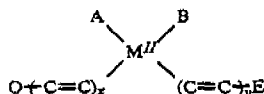
The preferred class of materials used include platinum group metal oxidation states II and IV. Compounds in the lower (II) state of oxidation are preferred due to their function in generating the catalytic effect. A significant feature of the invention is the use of platinum group metal II coordination compounds having at least one coordination site occupied by a functional group containing an unsaturated carbon-to-carbon bond of the olefinic, acetylenic or aromatic pi bond configuration. Preferably, two or more of the coordination sites will be occupied by such functional groups since the stability and solubility in gasoline and diesel fuel of compounds having such multiple functional groups are improved. While not wishing to be bound to any particular theory, it is believed that such preferred compounds in the lowest possible oxidation state are the most beneficial for producing instantaneous catalytic effect.

Occupation of one or more coordination sites with the following unsaturated functional groups has been found useful:

1. Benzene and analogous aromatic compounds such as anthracene and naphthalene.
2. Cyclic dienes and homologues such as cyclooctadiene, methyl cyclopentadiene, and cyclohexadiene.
3. Olefins such as nonene, dodecene, and polyisobutenes.
4. Acetylenes such as nonyne and dodecyne.

These unsaturated functional groups, in turn, can be substituted with nonhalogen-substituents such as alkyl, carboxyl, amino, nitro, hydroxyl and alkoxy groups. Other coordination sites can be directly occupied by such groups.

The general formula for the preferred coordination II compounds is:



where M^{II} represents the platinum group metal, with a valence of +2, where A, B, D, and E are groups such as alkoxy, carboxyl, etc. described above, where $(\text{C} \equiv \text{C})_x$ and $(\text{C} \equiv \text{C})_y$ represent unsaturated functional groups coordinated with the platinum group metal, and where x and y are any integer, typically 1 to 5.

Platinum group metals include platinum, palladium, rhodium, ruthenium, osmium, and iridium. Compounds including platinum, palladium and rhodium, especially platinum in combination with palladium and/or rhodium, are preferred in the practice of this invention.

Fuel additives containing platinum coordination compounds containing platinum in an amount of at least 10% of the total weight of all platinum group metals are preferred. Particularly good results have been achieved with additives containing a platinum coordination compound in combination with a palladium compound or palladium and rhodium compounds. Preferred weight ratios of platinum to palladium to rhodium are within the range of from 1:1:1 to 1:10:0.5.

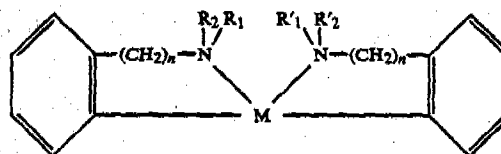
The most preferred platinum group coordination compounds are those represented by the following formula:



wherein X is a cyclooctadienyl ligand; M is a platinum group metal; and R is benzyl, phenyl or nitrobenzyl.

Among other suitable platinum group metal compounds, especially palladium compounds, are the following which include at least one sigma or pi carbon to platinum group metal bond.

(a) 2,2'-bis(N,N-dialkylamino)1,1'-diphenyl metals, as represented by the formula



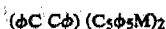
Wherein M is a platinum group metal; R₁ and R₂ are lower alkyl, e.g., from 1 to 10 carbons; and n is an integer from 1 to 5. Representative of this group is 2,2'-bis(N,N-dimethylamino)1,1'-diphenyl palladium.

(b) tetrakis (alkoxy carbonyl) metal cycloalkenes, as represented by the formula



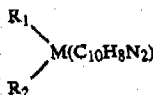
wherein M is a platinum group metal; R₁ is a lower alkyl, e.g., from 1 to 5 carbons; and R₂ is a cycloalkene having, e.g., from 5 to 8 carbons and from 2 to 4 unsaturations within the ring structure. Representative of this group is tetrakis (methoxy carbonyl) palladium cyclopentadiene.

(c) μ -diphenyl acetylene bis (η^5 -pentaphenyl cyclopentadiene) di metals as represented by the formula



wherein M is a platinum group metal and ϕ is phenyl. Representative of this group is μ -diphenyl acetylene bis (η^5 -pentaphenyl cyclopentadiene) dipalladium.

(d) dialkyl dipyridyl metals of the formula



wherein M is a platinum group metal; and R₁ and R₂ are lower alkyl, e.g., having from 1 to 5 carbons. Representative of this group is diethyl dipyridyl palladium.

(e) bis (π -allyl) metals of the formula



wherein M is a platinum group metal and R is hydrogen, aryl or alkyl, e.g., one to ten carbons. Representative of this group is bis (phenyl allyl) palladium.

The platinum group metal compound will be added to gasoline in an amount effective to improve engine performance in terms of operating efficiency or emissions reduction. Typically, the compound will supply an amount of the metal within the range of from 0.01 to

13

the scope of the present invention which is defined by the following claims.

We claim:

1. A method of reducing emissions from or increasing the utilizable energy of gasoline for powering internal combustion engines, comprising admixing with gasoline a fuel soluble organo-metallic fuel additive composition in an amount effective to supply from 0.01 to 1.0 parts per million of platinum per part of fuel, said composition comprising a compound having the general formula



wherein X is a ligand containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration and R_1 and R_2 are, independently, benzyl, phenyl, nitrobenzyl or alkyl having from 1-10 carbons.

2. The method of claim 1 wherein X is a dipyridyl or cyclooctadienyl ligand.

3. The method of claim 1 wherein R_1 and R_2 are both methyl, phenyl or benzyl.

4. The method of claim 1 wherein said fuel additive composition further comprises a fuel-soluble solvent for said platinum compound.

5. The method of claim 4 wherein said platinum and said solvent are present in amounts sufficient to supply oxygen and metal at a weight ratio of from 1,000:1 to 100,000:1.

6. The method of claim 5 wherein said solvent is an alcohol having from one to four carbon atoms and is employed at a level of from 0.25 to about 5 percent by weight of the fuel.

7. The method of claim 4 wherein said alcohol is ethanol employed at a level up to about 1 percent of said composition and said platinum is present at a level of from 0.05 to 0.5 parts per million parts fuel.

8. The method of claim 4 wherein said solvent comprises ethanol, tetrahydrofuran, methyl tertiary butyl ether, or combinations of these.

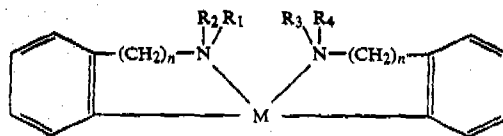
9. The method of claim 8 wherein R_1 and R_2 each comprise benzyl and said solvent comprises ethanol.

10. The method of claim 8 wherein R_1 and R_2 each comprise nitrobenzyl and said solvent comprises tetrahydrofuran.

11. The method of claim 8 wherein said solvent comprises methyl tertiary butyl ether.

12. A method of increasing the utilizable energy of gasoline for powering internal combustion engines, comprising admixing with gasoline a fuel soluble organo-metallic fuel additive composition in an amount effective to supply from 0.01 to 1.0 parts per million of platinum group metal per part of fuel, said composition comprising compounds selected from the group consisting of 2,2'-bis (N, N-dialkylamino) 1,1'-diphenyl metals of the general formula

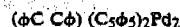
14



wherein M is platinum, palladium, rhodium or iridium; R_1 - R_4 are, independently, alkyl having from 1-10 carbons; and n is an integer from 1-5; tetrakis (alkoxy carbonyl) metal cycloalkenes of the general formula



wherein M is a platinum, palladium, rhodium or iridium; R_1 is alkyl having from 1-5 carbons; and R_2 is cycloalkene having from 5-8 carbons and from 2-4 unsaturations in the ring structure; bis(cyclopentadiene) acetylene dipalladium compounds of the general formula



wherein ϕ is phenyl; dialkyl dipyridyl metals of the formula



wherein R_1 and R_2 are alkyl having from 1-10 carbons; and M is platinum, palladium, rhodium or iridium; and bis (π -allyl) metals of the general formula



wherein M is platinum, palladium, iridium and rhodium; and R is hydrogen, aryl or alkyl having from 1-10 carbons.

13. The method of claim 12 wherein said compound is selected from the group consisting of 2,2'-bis (N,N-dimethylamino) 1,1'-diphenyl palladium; tetrakis (methoxy carbonyl) palladia cyclopentadiene; μ -diphenyl acetylene bis (η^5 -pentaphenyl cyclopentadiene) dipalladium; and bis (phenyl allyl) palladium.

14. The method of claim 12 wherein said fuel additive composition further comprises a fuel-soluble solvent for said metal compound.

15. The method of claim 14 wherein said metal and said solvent are present in amounts sufficient to supply oxygen and metal at a weight ratio of from 1,000:1 to 100,000:1.

16. The method of claim 15 wherein said solvent is an alcohol having from one to four carbon atoms and is employed at a level of from 0.25 to about 5 percent of the weight of the fuel.

17. The method of claim 16 wherein said alcohol is ethanol employed at a level up to about 1 percent of said composition and said metal is present at a level of from 0.05 to 0.5 parts per million parts fuel.

18. The method of claim 14 wherein said solvent comprises ethanol, tetrahydrofuran, methyl tertiary butyl ether, or combinations of these.

* * * * *

METHOD AND APPARATUS FOR IMPROVING COMBUSTION, THERMAL EFFICIENCY AND REDUCING EMISSIONS BY TREATING FUEL

RELATED APPLICATIONS

This application is a Continuation-In-Part of copending U.S. application Ser. No. 746,551, filed June 19, 1985, now abandoned which in turn is a continuation of U.S. application Ser. No. 516,094, filed July 22, 1983, now abandoned.

BACKGROUND OF THE INVENTION

It has been suggested that certain advantages can be attained by the controlled introduction of catalytic materials into combustion chambers along with the air, fuel and other fluids introduced. (See U.S. Pat. Nos. 2,460,700 to Lyons; 3,862,819 to Wentworth; 4,014,637 to Schena and 4,214,615 to Boyer and see British Pat. Nos. 1,381,936 and 1,191,464.)

Steam or air atomization of catalyzed fuel just prior to its introduction into combustion chambers has also been suggested in U.S. patent application Ser. No. 473,951 to Osgerby, filed Mar. 10, 1983 which application is assigned to the assignee of the present application.

Fuel oils and other carbonaceous fuels in liquid form such as coil-oil or coal-water slurries for industry and home use vary in viscosity, BTU value, specific gravity, flash point and other characteristics including sulfur content. Such fuels also vary in price making it desirable to burn the cheaper fuels provided desired burning characteristics and emissions requirements can be met.

Less expensive heavier fuel oils, commonly referred to as #4 or #6, have the advantage of having higher BTU values than the lighter distillate (e.g., #2) fuel oils. Unfortunately, these heavier and cheaper fuels do not burn as completely or cleanly as the more expensive lighter distillate fuels. Specifically, heavier fuels have lower combustion efficiencies and higher particulate emissions than do lighter fuels. The industry has been aware that treating cheaper fuels to burn with characteristics of more expensive fuels is desirable provided treatment costs are low; however, prior fuel treatments have been unsatisfactory for most applications.

SUMMARY OF THE INVENTION

Broadly, the present invention is a method and apparatus for treating liquid fuels comprising preparing a liquid medium by metering a controlled amount of an active precious metal catalyst such as a platinum group metal, into an emulsifying liquid such as water. The liquid medium, along with stabilizing agents (if necessary for storage stability), is then mixed through agitation, collision, shearing, homogenization or other turbulent means with liquid fuel to produce an emulsion suspension which is delivered under pressure to the combustion chamber for burning. Mixing of the liquid fuel, liquid medium and catalyst may be accomplished by first mixing any two together and then adding the third, or by mixing all three at once.

It is a feature that the emulsion suspension may be stored for substantial lengths of time after such treatment.

It is a further feature that the following benefits are obtained by the fuel treatment of the present invention:

1. Improved combustion and thermal efficiency;

2. Reduced flue gas emissions (particulates and pollutants);
3. Reduced fireside fouling rate;
4. Suppression of NO_x and SO₃ production; and
5. Decreased minimum excess air capability.

It is also a feature of the invention that, due to the enhanced combustibility of the emulsified suspension, the capability exists to utilize cheaper liquid fuel in lieu of the more expensive light distillate fuels. That is accomplished with minor and inexpensive equipment modifications to combustion systems originally designed to burn light distillate fuels exclusively, and without the deleterious environmental consequences usually associated with burning heavier fuel oils.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of an on-site fuel treating arrangement and a bulk terminal facility treating and delivering arrangement.

FIG. 2 shows a catalyst metering device for use in preparing the aqueous catalyst medium.

FIG. 3 is a schematic of a boiler having a flame zone in the combustion chamber, the combustion air and fuel supply systems, and equipment for treating fuel oil prior to burning.

FIG. 4 is a plan view of a flame zone in the burner illustrating the formation of droplets and micro-explosions as the fuel emulsion suspension is injected into the chamber and burned therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The methods and apparatus for treating, storing, and burning the emulsion suspension sometimes herein referred to as catalyzed emulsified fuel oil (or CEFO) are further understood by turning to FIG. 1 in which the end user's burner 10 is supplied with the emulsion suspension (CEFO) in two alternative ways. First, production of CEFO is accomplished in-line at the end-user's facility and, secondly production of CEFO is done at a remote bulk terminal facility for later transportation to an end user's facility. The end user's furnace combustion chamber 10 is supplied with CEFO as continuously prepared or as supplied from the user's CEFO storage tank. Untreated fuel oil stored in an oil tank 12 is led via oil feed-line 13 to emulsifier mixer 14. Simultaneously emulsifier mixer 14 is supplied with catalyzed water through water feed-line 16. Catalyst metering device 17 meters into the water in water line 16 controlled amounts of precious metal catalyst. Emulsifier 14 includes a control mechanism for controlling the ratio of water to fuel supplied to the emulsifier. The aqueous catalyst medium and fuel oil flow into emulsifier 14 where an emulsion suspension of fuel oil, water, and catalyst is produced. This emulsion suspension is then delivered to combustion chamber 10 along CEFO feed-line 18 for burning.

Alternatively, CEFO is produced and delivered by truck or other conveyance to the end-user. Turning again to FIG. 1, fuel from the supplier's storage tank 21 and an aqueous catalyst from catalyst unit 23 are supplied to and treated in emulsifier 22. Catalyst unit 23 adds selected quantities of catalyst to the water as it flows to emulsifier 22. CEFO formed in emulsifier 22 may be directed to longer term storage tank 25 or directly to shorter term rack storage 26. From rack 26, CEFO is loaded onto truck 27 for delivery to the end-

3

user's CEFO tank 11. CEFO in storage tank 25 is supplied as needed to rack 26 for future delivery.

Turning to FIG. 2 catalyst metering device unit 17 is shown in detail. Unit 23 has similar construction. Water enters unit 17 in line 30 and passes through check valve 31 to static mixer 32. From static mixer 32 the flow in line 30 continues through flow sensor 33 and finally exits via line 30. Catalyst is added in controlled amounts at a tee section 36 located in and forming a part of line 30. Precious metal catalyst is stored in a liquid in catalyst reservoir 37. Metering pump 38 supplies the catalyst liquid via tube 39 to mixing tee section 36 where the catalyst liquid is injected into the exit water line 30. Further mixing of the flowing water and the liquid catalyst is accomplished in in-line static mixer 32. Flow sensor 33 is electrically connected to pump pulser 42, which in turn is electrically connected to pump 38. In operation, the rate of flow through flow sensor 33 sends signals to pulser 42 which in turn controls the rate of pulsing of the metering pump 38 to increase or decrease the rate of flow of liquid catalyst to the water flowing through line 30. Calibration of the device is a function of varying the catalyst concentration in reservoir 37.

Catalyst material may be added as part of a liquid medium to the fuel or to emulsion as formed at any location prior to entry into the combustion chamber. Catalyst material may also be added in solid form provided mixing is adequate and provided that ranges of fuel to emulsifying liquid to catalyst are maintained.

In some instances, when substituting CEFO for lighter distillate fuel oils, burner equipment changes are necessitated. Specifically, it is often necessary to modify (retrofit) existing plant systems by the addition of an in-line fuel oil preheater and, in addition, add or substitute motors, pumps, nozzles, in-line oil filters and regulators used to measure flow rates and pressures.

FIG. 3 shows a furnace and attendant air and fuel supply system, combustion unit 51, burner nozzle assembly 52, fuel supply line 53, air supply fan 55 and duct 56. CEFO under action of the pump 57 is supplied from emulsifier 58 via line 53 through filter 60 and preheater 61. The emulsifier 58 is supplied with fuel oil from tank 62 and with liquid catalyst medium from catalyst unit 63. The CEFO may be heated in preheater 61 to temperatures in the range of 100°-220° F. and preferably in the range of about 120° F. to about 150° F. This burner system which was designed and operated to burn No. 2 fuel required the following modification to refit it for the more viscous No. 4 fuel:

1. addition of a preheater;
2. larger capacity pump (and larger motor to drive the pump);
3. new filter; and
4. new burner nozzle.

Turning now to FIG. 4 primary flame zone 71 in combustion chamber 72 is shown wherein the CEFO has been atomized as introduced via burner nozzle 73 into the hot chamber 72. Fuel oil droplet components 74 are shown enlarged as circles. Enlarged circles with blackened centers 76 illustrate water droplet components with catalyst therein. Interspersed amongst the fuel oil droplets and water droplets are micro-explosions of water droplets 77.

Through absorption of heat from the combustion flame, aqueous droplets are rapidly transformed from a liquid to a vapor state, creating micro-explosions 77 within combustion chamber 72. The intensity of the

4

vaporization process creates pressure differentials, which in turn shatter the surrounding fuel oil into smaller droplets 76 thereby enhancing the efficiency and completeness of the combustion reaction.

At the site of each micro-explosion 77, the heat of combustion causes rapid dissociation and activation of the precious metal catalyst within the primary flame zone. This method of introduction of catalyst into the primary flame zone 71 ensures consistent optimal utilization of and realization of the beneficial effects derived from the active precious metal catalysts.

In tests performed to date, CEFO has been successfully burned under various operating conditions. It has been discovered that stable emulsions of oil and emulsifying liquid including water, in the range of about 3% by volume to about 15% by volume of emulsifying liquid to fuel oil, are useful in the practice of the invention. While the amount of emulsifying liquid used varies with the fuel used, it is necessary to use an amount of emulsifying liquid to create and maintain a stable emulsion. Among the factors used in determining the appropriate ratio of water to fuel oil is the viscosity of the base fuel oil. Fuel oils with a viscosity in excess of 60 SSU can be treated to form a stable homogenous emulsion. It has also been determined that the optimum water droplet size in the combustion chamber falls in the range of one to ten microns.

Data collected during CEFO testing has revealed the beneficial improvements directly attributable to the use of precious metal catalyst. Tests were performed using concentrations of small amounts of catalyst in the range of 0.005 ppm-0.5 ppm catalyst to fuel oil measured as catalyst metal on a weight basis. The preferred amount of catalyst to fuel oil fell within the range of about 0.02 to about 0.06 ppm by weight.

Among the noble metal catalysts useful in the practice of the present invention are:

- ruthenium (IV) oxide
- ruthenium (III) chloride
- ruthenium (III) chloride trihydrate
- ruthenium (III) bromide, and its hydrates
- ammonium aquopentachlororuthenium (III), $(\text{NH}_4)_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$
- potassium ruthenium (VI) oxide
- rhodium (III) oxide
- rhodium (III) chloride, and its hydrates
- rhodium (III) nitrate, and its hydrates
- iridium (III) chloride
- iridium (III) oxide
- iridium (IV) oxide
- hydrogen hexachloroiridium (IV), and its hydrates
- ammonium hexachloroiridium (IV), and its hydrates
- osmium tetroxide
- osmium (III) chloride
- platinum black
- platinum (IV) oxide, and its hydrates
- platinum (II) chloride
- platinum (IV) chloride
- hydrogen hexachloroplatinum (IV) hydrate
- hydrogen hexahydroxoplatinum (IV)
- tetraammineplatinum (II) chloride monohydrate
- dinitritodiammineplatinum (II)
- dihydrogen sulphatodinitrito platinum (II)
- tetraammineplatinum (II) dinitrate
- palladium (II) chloride
- palladium (II) oxide
- palladium (II) nitratedihydrate
- ammonium hexachloropalladium (IV)

4,629,472

5

tetraamminepalladium (II) nitrate
 potassium tetracyanopalladium (II) trihydrate
 potassium perrhenate
 rhenium (III) chloride
 tris (acetyl acetonate) rhenium (III)
 cis-Dichloro(2,2'-bipyridine)platinum (II), PtCl₂
 (C₁₀H₈N₂)
 dichloro(1,5-cyclooctadiene)platinum (II), PtCl₂
 (C₈H₁₂)
 2-hydroxyethanethiolato(2,2',2''-terpyridine)platinum (II) nitrate, [Pt(C₂H₅OS)(C₁₅H₁₁N₃)]NO₃
 tricarbonylchloro iridium (I), [IrCl(CO)₃]_n
 chloro(1,5-cyclooctadiene)iridium (I) dimer
 [IrCl(C₈H₁₂)₂]
 trans-dichlorobis(ethylenediamine), iridium (III) chloride, trans-[IrCl₂(C₂H₈N₂)₂]Cl
 rhodium (II) octanoate dimer, Rh₂[O₂C(CH₂)₆CH₃]₄
 acetylacetonato(1,5-cyclooctadiene), rhodium (I), Rh(C₈H₁₂)(C₅H₇O₂)
 acetylacetonato(norbornadiene), rhodium (I), Rh(C₇H₈)(C₅H₇O₂)
 hydridotetrakis(triphenylphosphine), rhodium (I), RhH(PPh₃)₄
 diacetatobis(triphenylphosphine), palladium (II) (CH₃CO₂)₂Pd(PPh₃)₂
 Bis(dibenzylideneacetone), palladium (O) Pd(C₁₇H₁₄O)₂
 Dichloro[1,2-bis(diphenylphosphino)ethane]palladium (II) PdCl₂(Ph₂PCH₂CH₂PPh₂)
 Palladium (II) trifluoroacetate Pd(CF₃CO₂)₂
 Acetatohydridotris(triphenylphosphine)ruthenium (II) RuH(OCOCH₃)(PPh₃)₃
 Bis(benzene)dichlorodi-μ-chlorodiruthenium (II) [RuCl₂(C₆H₆)₂]
 Tris(2,2'-bipyridine)ruthenium (O) (C₁₀H₈N₂)₃Ru
 Carbonyldihydridotris(triphenylphosphine)ruthenium (II) RuH₂(CO)(PPh₃)₃
 Bis(cyclopentadienyl)ruthenium (II) "Ruthenocene" (C₅H₅)₂Ru
 Dihydridotetrakis(triphenylphosphine)ruthenium (II) RuH₂(PPh₃)₄
 Ruthenium(III)hexafluoroacetylacetonate Ru(CF₃COCHCOF₃)₃
 Dichloroethylenediammineplatinum (II) [Pt(C₂H₈N₂)Cl₂]
 Bis(acetylacetonato)platinum (II) [Pt(C₅H₇O₂)₂]
 Dichlorobis(triphenylphosphine)platinum (II) [PtCl₂(PPh₃)₂]
 Tetrakis(triphenylphosphine)platinum (O) [Pt(PPh₃)₄]
 Bis(acetylacetonato)palladium (II) [Pd(C₅H₇O₂)₂]
 Dichloro(cycloocta-1,5-diene)palladium (II) [Pd(C₈H₁₂)Cl₂]
 Chloro(π-allyl)palladium (II) dimer [Pd(π-C₃H₅)Cl]₂
 Palladium (II) acetate trimer [Pd(CH₃CO₂)₂]₃
 Tris(acetylacetonato)ruthenium (III) [Ru(C₅H₇O₂)₃]
 Hydridocarbonyltris(triphenylphosphine)rhodium (I) [Rh(H)(CO)(PPh₃)₃]
 Acetylacetonatodicarbonylrhodium (I) [Rh(CO)₂(C₅H₇O₂)]
 Tris(acetylacetonato)rhodium (III) [Rh(C₅H₇O₂)₃]
 Bromotris(triphenylphosphine)rhodium (I) [RhBr(PPh₃)₃]
 Rhodium (II) acetate dimer [Rh₂(CO₂CH₃)₄]
 Tris(acetylacetonato)iridium (III) [Ir(C₅H₇O₂)₃]
 Dodecacarbonyltriosmium (O) Os₃(CO)₁₂

While the above mentioned precious metal catalysts are preferred, other metal catalysts, both organo-metal-

6

lic and inorganic-metallic can be employed in the present invention. Catalysts insoluble or insoluble in the emulsifying liquid may be used.

EXAMPLE I

A homogeneous emulsion fuel was burned in a 300 HP fine tube boiler set at its maximum firing rate of 112 gph, fuel—#6, emulsion—3.2% water by volume, catalyst—0.05 ppm by weight, preheated emulsion temperature—130° F.

Results: When burning the catalyzed homogenized emulsion fuel, the minimum excess air capability of the combustion system was reduced by an average of 1.8%, as compared to normal operating conditions. This was accomplished without any detectable increase in stack carbon monoxide emissions. Stack gas temperatures were reduced by approximately 16° F. See Table I, Runs I and II.

TABLE I

	Oxygen A	Oxygen B	% CO	Exit Temp.
Run I	2.3%	1.9%	0	722
	1.8	1.6	0	728
	1.7		0	
	1.6	1.4	.01%	720
	1.5		.01±	
	1.4		.02	712
Run II	5.4	4.3	0	
	2.1	1.8	0	
	1.8	1.6	0	
	1.6	1.5	0 to .01%	712

Table I Key

O₂A= readings from catalytic type oxygen analyzer with probe in the exhaust duct.
 O₂B= readings from zirconium oxide type oxygen analyzer with probe in the exhaust duct reading "net" flue gas on a "wet" basis.
 %CO= stack gas measured using Enerac instrument with its probe inserted in the exhaust duct.
 Exit Temp.= stack gas temperature in degrees F.

EXAMPLE II

A catalyzed emulsion fuel was burned in a forced hot air residential furnace rated at 1 gph, equipped with a Wayneburner.

Fuel—#4

Emulsion—3% and 6% water by volume

Catalyst Concentration—0.03 ppm by weight

Burner rated—1-6 gph

Preheated emulsion temperature range—120°-220° F.

Firing rate—1.25 gph

Modifications to system

1. Oil pump was replaced with a pump of higher capacity;
2. 1/6 HP burner/pump motor was replaced with a 0.25 HP burner/pump motor;
3. An in-line immersion type fuel oil preheater was installed in the homogenized emulsion feed line; and
4. String type element oil filters were replaced with strainer type oil filters.

Results: A consistent 4% average increase in thermal efficiency, and an average 300° F. increase in flame temperature (above normal operating conditions) were

observed. Stack smoke emissions remained relatively constant. See Table II, Runs I and II.

TABLE II

Emulsion	T _o	T _f	T _{st}	CO ₂	O ₂	% Effi- ciency	Smoke	P _o
<u>Run I:</u>								
6% water .03	120	1900	700	7.7	10.8	66.	4.	100
ppm cat	160	2100	735	8.5	9.9	67.6	3.	100
	140		765	8.6	9.8	66.4	4.	100
<u>Run II:</u>								
3% water .03	230	1900	655	7.9	10.6	68.7	4.	100
ppm cat	180							
	160		671	8.7	9.8	70.6	4.	100
	150	2100	672	8.8	9.5	70.3	4.	100
	120		674	8.8	9.6	70.1		100

Table II Key

Temperatures were measured with thermocouples.

T_o=emulsion preheat temperature

T_f=flame temperature (firebox)

T_{st}=exhaust duct temperature (ENERAC)

Gas composition was measured using an ENERAC (P50) instrument with the probe in the exhaust duct;

Thermal efficiency was indicated by the ENERAC instrument;

Smoke was measured using a Bacharach pump/filter and comparator chart; and

P_o=emulsion pressure at the burner measured in pounds per square inch.

EXAMPLE III

A combustion burner system was operated using two fuels for comparison. First, the system was fired with normal (i.e., untreated) #4 fuel oil. Next, the same unit was fired with a #4 catalyzed emulsion fuel oil (CEFO).

Fuel—#4 (treated and normal)

Emulsion—3.8% water by volume

Catalyst concentration—0.038 ppm by weight

Burner firing rate—1.25 gph

Preheated emulsion temperature range—140°–180° F.

Results: The catalyzed emulsion fuel showed significantly improved combustion characteristics when compared to untreated #4 fuel oil. Average improvements were:

1. percent thermal efficiency increased 7.1%;
2. average flame temperature increased 247° F.;
3. average stack gas temperature decreased 136° C.;
4. O₂ readings decreased an average of 2.6%;
5. average CO₂ readings increased 2.1%; and
6. stack smoke emissions remained relatively constant (see Tables III and IIIA).

TABLE III

Test	T _o	T _f	T _{st}	CO ₂	O ₂	% Effi- ciency	Smoke	P _o
#4	170	2050	730	11.4	6.2	73.9	4.	100
	180	1900	680	9.5	8.6	71.5	3.	75
#4	170	2100	720	11.3	6.4	73.8	3.	100
	170	2100	694	11.7	6.	75.1		100
#4	175	200	670	9.7	8.5	72.5	3	75
	170	2050	630	10.4	7.6	74.5	3	75

TABLE IIIA

Test	T _o	T _f	T _{st}	CO ₂	O ₂	% Effi- ciency	Smoke	P _o
5 3% water with cat.	140	2300	530	13.3	3.8	81.9	4	100
	180	2250	502	12.3	5.3	81.6	3	100
	150	2300	585	13.1	4.1	80.3	3	100
	175	2250	575	12.1	5.4	79.4	4	100
	140	2300	563	12.7	4.6	80.2	5	100

Tables III and IIIA Key

T_o=oil preheat temperature

T_f=flame temperature

T_{st}=exhaust duct temperature

P_o=emulsion or fuel oil pressure at the burner measured in pounds per square inch

Smoke=Bacharach Number.

EXAMPLE IV

A 250 HP fire tube boiler was operated using three fuels for comparison. First, light distillate #2 fuel oil was fired in the combustion unit. Next, the same unit was fired using #4 fuel oil and water in emulsion form. Lastly, the unit was fired with #4 catalyzed emulsion fuel.

Fuels

#2 untreated

#4 with 6.2%, 6.3% and 8% water (by volume)

#4 with 2.8% and 3.5% water plus catalyst

Catalyst—concentration 0.51 ppm (by weight)

Burner firing rates—High (60 gph); Medium (20–30 gph)

Results: Improvements over #2 oil firing (averages):

High Fire: 6% emulsion; 2.1% increase in lbs. steam/gallon of oil 2% catalyst emulsion; 7.7% increase in lbs. steam/gallon of oil.

Medium Fire: 8% emulsion; 2.9% increase in lbs. steam/gallon of oil 3.5% catalyst emulsion; 11.9% increase in lbs. steam/gallon of oil

(see Table IV).

TABLE IV

Comparison of Performance #2 vs. Emulsion Fuels and Catalyst								
Firing Rate	Fuel	Emul- sion	Cata- lyst	Com- bustion effi- ciency	% O ₂	Smoke	lbs. steam/ gallon oil	
High	#4	6.2%	No	88.	3.	4.	114.7	
	#4	6.3	No	87.4	5.4	2.	111.7	
	#4	2.8	Yes	87.9	2.2	1/2.	118.2	
	#2	No	No	87.7	3.5	4.	112.3	
	#2	No	No	87.3	4.8	3.	107.2	
Medium	#4	8.0	No	84.9	9.6	3.	96.6	
	#4	3.5	Yes	89.2	2.1	1/2.	105.1	
	#2	No	No	83.	11.1	2/3.	93.9	

What is claimed is:

1. A method of improving the combustion of fuel in a chamber by treating the fuel to form a suspension comprising:

(a) mixing with such fuel a quantity of emulsifying liquid to form a stable suspension; and

(b) adding a small amount of precious metal catalyst so that such metal is present in such suspension prior to its introduction into such chamber.

2. The method of claim 1 in which the catalyst metal is first mixed with a liquid and introduced into the fuel to cause the catalyst to be present in the suspension.

3. The method of claim 1 in which the catalyst metal is first mixed with a liquid and introduced into the emulsifying liquid which in turn is mixed with the fuel.

4. The method of claim 1 in which the catalyst metal is first mixed with a liquid and then introduced into the formed suspension.

5. The method of claim 1 in which the catalyst metal in solid form is introduced into the fuel.

6. The method of claim 1 in which the catalyst metal in solid form is introduced into the emulsifying liquid.

7. The method of claim 1 in which the catalyst metal in solid form is introduced into the formed suspension.

8. The method of claim 1 in which the emulsifying liquid is water.

9. A method of improving the combustion of fuel in a chamber by treating the fuel to form a suspension comprising:

(a) admixing with a quantity of emulsifying liquid a small amount of precious metal catalyst to form a liquid catalyst medium;

(b) mixing the liquid catalyst medium with the fuel under turbulent conditions to form a stable suspension of fuel, emulsifying liquid and catalyst; and

(c) thereafter introducing the suspension into the chamber for combustion therein.

10. The method of claim 9 in which the quantity of emulsifying liquid is about 3% to about 15% by volume to the fuel and the small amount of precious catalyst added to form the catalyst medium is an amount sufficient to provide from about 0.005 ppm to about 0.5 ppm catalyst metal by weight in the said suspension.

11. The method of claim 9 in which the small amount of precious metal catalyst added to form the catalyst

medium is an amount sufficient to provide about 0.02 ppm to about 0.06 ppm catalyst metal in said suspension.

12. The method of claim 9 in which the suspension is stored for a substantial period of time.

13. The method of claim 9 in which the suspension is heated prior to its introduction into the chamber.

14. A treated liquid fuel comprising an emulsified suspension of

(a) about 85% to about 97% by volume liquid carbonaceous fuel;

(b) about 15% to 3% water; and

(c) about 0.005 ppm to about 0.5 ppm precious catalyst metal by weight.

15. A method of improving the combustion of fuel in a chamber by treating the fuel to form a suspension comprising:

(a) mixing with such fuel at least 3% by volume of an emulsifying liquid to form a stable suspension; and

(b) adding a small amount of precious metal catalyst so that such metal is present in such suspension prior to its introduction into such chamber.

16. A method of improving the combustion of fuel in a chamber by treating the fuel to form a suspension comprising:

(a) admixing with at least 3% by volume of an emulsifying liquid a small amount of precious metal catalyst to form a liquid catalyst medium;

(b) mixing the liquid catalyst medium with the fuel under turbulent conditions to form a stable suspension of fuel, emulsifying liquid and catalyst; and

(c) thereafter introducing the suspension into the chamber for combustion therein.

* * * * *

35

40

45

50

55

60

65