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SUPERINDUSTRIA Y COMERCIO

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JEFE DE DIVISIÓN DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

E.

S.

D.

REF: Expediente No. 02 042.848 – solicitud de patente de invención
a favor de DYNO NOBEL, INC.

Respuesta a oficio No. 10638 del 10 de noviembre de 2005

JUAN PABLO CADENA SARMIENTO, portador de la tarjeta profesional No. 57.492 del C.S.J., obrando como apoderado sustituto de la sociedad DYNO NOBEL, INC., según lo acredita el documento de sustitución de poder presentado en esa División, me permito dar respuesta a las observaciones de carácter técnico y jurídico, relacionadas con la patentabilidad, para la concesión de la patente de acuerdo con la Decisión 486 según el concepto técnico No. 1758 notificado por fijación en lista de fecha 10 de noviembre de 2005, cuyo término fue prorrogado mediante escrito radicado el 01 de febrero de 2006.

Atendiendo a las observaciones del señor examinador respecto a la claridad de la solicitud nos permitimos presentar una nueva descripción y un nuevo capítulo reivindicatorio de 1 – 21 reivindicaciones los cuales reemplazan completamente los anteriormente presentados.

El señor examinador objeta la claridad de la descripción por las siguientes razones:

- En el folio 11, el empleo de la frase “selección de un agente detonante emulsionado predeterminado” torna confusa la memoria descriptiva,

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pues no especifica el objeto de la solicitud. Dice el señor examinador que es más claro emplear frases que en la misma solicitud se usan posteriormente.

Al respecto es necesario remitir al señor examinador a la nueva descripción corregida adjunta, en la cual, en el segundo párrafo de la página 1 se ha corregido el término "emulsión" por su traducción más correcta: "emulsionado". Con esta modificación y la definición que se presenta a continuación es innecesario realizar la modificación sugerida por el señor examinador, ya que para el técnico con habilidad en la materia queda suficientemente claro el significado de la expresión "agente detonante emulsionado". Por otro lado, de la lectura de la solicitud es claro que el objeto de la misma no es la "selección de un agente detonante predeterminado", sino la adición de un agente reductor de energía a dicho agente detonante predeterminado; por lo que realizar la modificación solicitada por el señor examinador no aclararía la memoria descriptiva sino que, por el contrario, la tornaría aun más oscura ya que no sería claro si lo que se desea proteger, es el agente detonante emulsionado o la adición del agente reductor de energía.

- Prosigue el señor examinador afirmando que el mismo párrafo no es claro cuando se habla del paso de "transporte de un agente detonante emulsionado". Un técnico medio se cuestiona inmediatamente a que se refiere a ese transporte, ¿De un sitio de almacenamiento a un sitio de mezcla? ¿De un tanque al fondo del pozo?, Etc.

Para superar esta objeción del señor examinador, la nueva descripción corregida adjunta elimina este paso de dicho párrafo.

- Prosigue el señor examinador diciendo que se habla de agregar un

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agente reductor de energía a la emulsión mientras se transporta. Pero tampoco es claro como se hace para hacer la mezcla mientras se esta transportando, y mucho menos como se hace para que quede en forma uniforme y homogénea.

En primer lugar, la descripción corregida adjunta cambia el término "emulsión" por "agente detonante emulsionado" que corresponde a una traducción más fiel del documento original en inglés; segundo, para superar esta objeción, como en el párrafo anterior, se ha eliminado cualquier referencia al transporte de la solución. Solo a modo de referencia, se desea aclarar que a partir de lo dicho en la parte de los antecedentes, queda claro para el técnico con habilidad en la materia que dicho transporte corresponde al transporte, desplazamiento o conducción del agente detonante emulsionado desde el sitio de almacenamiento al lugar donde va a ser utilizado. Así mismo, como es bien sabido por el técnico con habilidad en la materia, el agente reductor de energía se puede adicionar en un punto específico de la línea de bombeo, para permitir que mientras el agente detonante emulsionado y el agente reductor de energía se desplazan por la línea de bombeo las características físicas del agente detonante emulsionado, en otras palabras la presencia de gránulos y agentes reductores de densidad como esferas de vidrio, hagan que este se comporte como un lecho fluidizado y la turbulencia logre la mezcla uniforme y homogénea de ambos agentes.

- Dice el señor examinador que en el folio 16 se habla de un agente reductor de energía y en un momento dado se comienza a hablar de reductor de densidad (sic). Si bien un agente reductor de densidad podría ser reductor de energía, esto no necesariamente es siempre cierto y deja la descripción confusa.

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Al respecto remitimos al señor examinador al párrafo que va del final de la página 7 al comienzo de la página 8 de la descripción anexa, en el cual se habla de agentes gasificantes y de otros agentes reductores de la densidad. Para el técnico con habilidad en la materia es perfectamente claro que la adición de un agente gasificante a una solución líquida o parcialmente líquida, ocasiona la inmediata reducción de su densidad. El párrafo objetado por el señor examinador dice:

"Los métodos de la presente invención comprenden agregar un agente reductor de energía y preferentemente agentes gasificantes al agente detonante emulsionado mientras es transportado dentro de una perforación. (La frase "mientras es transportado" cubre la adición del agente reductor de energía ya sea corriente arriba o corriente abajo del medio de transporte usado, tal como una bomba para emulsión.) El término "transportado" incluye bombeado, extrusión u otros medios. Para voladuras perimetrales el agente reductor de densidad puede agregarse en cantidad suficiente como para reducir la energía del agente detonante emulsionado hasta un nivel que permita realizar la voladura perimetral obteniendo los resultados previamente descritos."

La referencia que se hace a la adición de los agentes reductores de la densidad tiene que ver con la práctica efectuada en el arte previo, donde en lugar de agregar los agentes reductores de energía de la presente invención, se agregan mayores cantidades de agentes reductores de densidad para lograr un efecto similar.

- Por último, el señor examinador dice que al describir el método de preparación del objeto de la solicitud, se habla que el agente reductor de

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energía se mezcla de forma uniforme y continua con la fase de emulsión mediante un mezclador dinámico, una válvula homogenizadora, un mezclador estático o tobera. Pero dado que el proceso no es claro, no se entiende en que punto se aplica. Se podría mezclar en un tanque previo, en la misma tubería de transporte, en un tanque posterior, en el mismo sitio de aplicación de la emulsión.

Esta objeción del señor examinador es completamente irrelevante. Dado que el objeto de la solicitud es proporcionar un agente detonante emulsionado mezclado con un agente reductor de energía y otros aditivos, el sitio donde se mezclen el agente detonante emulsionado con el agente reductor de energía no es tan determinante como el sitio donde se adicione el agente gasificante. Por lo tanto, que la mezcla del agente detonante emulsionado y el agente reductor de energía se lleve a cabo antes de bombearlo a su destino, dentro de la tubería de transporte, o en el sitio de destino carece completamente de importancia.

El señor examinador también objeta la claridad del capítulo reivindicatorio por las siguientes razones.

- No se encuentra correctamente redactado. Las reivindicaciones de método son totalmente confusas. El empleo de la frase "selección de un agente detonante emulsionado predeterminado" torna confusa la memoria descriptiva (sic), pues no especifica el objeto de la solicitud.

Como se dijo anteriormente, el objeto de la invención no es la naturaleza del agente detonante emulsionado, sino más bien el hecho de agregarle un agente reductor de energía a dicho agente detonante emulsionado, por lo que la frase en cuestión no afecta de forma alguna la claridad del

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huecas altamente resistentes para permitirle mantener una densidad específica deseada, aun cuando se someta a presiones elevadas como las que se encuentran a gran profundidad o bajo el efecto de una onda explosiva de una carga adyacente.

El objeto de dicha anterioridad es el que la formulación explosiva mantenga su sensibilidad al detonador a pesar de las presiones a las que se vea sometida. Dicha anterioridad no enseña o sugiere el uso de agentes reductores de energía, menos aun el uso de agua o de soluciones acuosas como las reivindicadas en la presente solicitud. Por lo tanto la presente solicitud es novedosa por sobre lo enseñado por la anterioridad D2.

- En cuanto a la altura inventiva, queremos llamara la atención del señor examinador hacia lo siguiente. Tanto la anterioridad D1 como la anterioridad D2 enseñan que es necesario reducir, de una forma u otra, la densidad de la emulsión explosiva para que se vuelva sensible a los detonadores utilizados normalmente en el arte, y agregarle microesferas huecas a la misma para que no pierda dicha sensibilidad al momento de ser sometida a diferentes presiones.

La presente solicitud enseña la necesidad de ajustar la energía explosiva de la emulsión detonante para lograr que, al momento de emplearla para volar paredes de roca, se formen trozos de roca de un tamaño específico. Para tal fin, los inventores de la presente solicitud emplean agua o soluciones acuosas de composición específica que se mezclan con composiciones explosivas existentes.

En otras palabras, la presente invención no enseña o sugiere un método para obtener un agente detonante emulsionado, lo que enseña es un

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método para reducir la energía explosiva de un agente detonante emulsionado.

Los agentes detonantes emulsionados son conocidos en el arte, los aditivos que se le agregan a dichos agentes con el fin de aumentar su sensibilidad también son conocidos en el arte, pero lo que el arte no conoce es el uso de agua o soluciones acuosas con el fin de controlar la energía explosiva de una emulsión detonante. El técnico con habilidad en la materia no podría derivar de forma obvia, a partir de las enseñanzas de D1 y D2, que adicionar agua o una solución acuosa a una formulación detonante en emulsión reduzca su energía explosiva al momento de la detonación.

Además, como es bien sabido en el arte, la adición de agua reduce la concentración de los agentes explosivos como el combustible o el nitrato de amonio, lo cual puede tener un efecto adverso sobre la sensibilidad del explosivo ya que sería necesario emplear sistemas de detonación más potentes y, por ende, más costosos que irían en detrimento del uso del método de la presente solicitud.

Por lo tanto, debido a que la presente solicitud enseña una formulación explosiva a la que se le ha reducido la energía y que, así mismo, conserva su sensibilidad a los detonantes convencionales, lo divulgado en la misma es claramente inventivo por sobre lo enseñado por los documentos D1, D2 y todos los ejemplos y documentos referenciados en dichas anterioridades.

- En conclusión, la presente solicitud es innegablemente novedosa e inventiva por sobre las anterioridades D1 y D2.

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Respetuosamente solicitamos por lo tanto, el retiro de la objeciones a la presente solicitud, sobre la base de los argumentos presentados y las reivindicaciones corregidas anexas las cuales no adicionan materia nueva, no afectan en ningún sentido el alcance de la invención y, en opinión del solicitante, cumplen con los requisitos de novedad, nivel inventivo y aplicabilidad industria exigidos por la Decisión 486.

De la Señora Jefe,

Atentamente,


JUAN PABLO CADENA SARMIENTO

T.P. No. 57.492 del C.SJ.

C.C. 80.410.337 de Usaquén

Carrera 7 No. 16-56 piso 9

Bogotá, Marzo 14 de 2006

CH/MEV/yg

Anexos

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X 1

AGENTE DETONANTE DE ENERGIA REDUCIDA Y METODO ASOCIADO

La presente invención se refiere a un agente detonante emulsionado de energía reducida preparado agregando un agente reductor de energía, preferiblemente agua o una solución acuosa, en cantidad suficiente para reducir la energía del agente detonante emulsionado hasta el nivel deseado. Esta invención se refiere también a un método para reducir la energía de un agente detonante emulsionado mientras se carga en una perforación, y a un método mejorado de voladura perimetral en el cual se agrega un agente reductor de energía a un agente detonante emulsionado, mezclándolo uniformemente con la emulsión mientras se bombea o se transporta dicha emulsión dentro de una perforación perimetral, para reducir la energía del agente detonante hasta el nivel deseado. Pueden controlarse además la densidad y la sensibilidad del agente detonante emulsionado agregando cantidades variables de agentes gasificantes.

ANTECEDENTES

Las composiciones detonantes emulsionadas son muy conocidas en este ramo. El término "emulsionado", en este caso, se refiere a una emulsión de agua en aceite compuesta por una solución de una sal inorgánica oxidante como fase discontinua y un combustible orgánico líquido como fase continua. Al sensibilizar la emulsión, esta se convierte en un agente detonante emulsionado.

Los agentes detonantes emulsionados son líquidos en su composición inicial, y pueden permanecer líquidos para ser bombeados, o se les puede dar mayor consistencia, que dependerá de la viscosidad del combustible orgánico líquido y de otros aditivos. Estos agentes detonantes pueden usarse ya sea a granel o en recipientes, y pueden bombearse en el lugar directamente a las perforaciones. Como alternativa, a una emulsión se le pueden añadir aditivos sólidos tales como gránulos de nitrato de amonio (AN), y de acuerdo a la cantidad de gránulos que se agregue, la mezcla resultante puede bombearse

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dentro de las perforaciones o inyectarse en las mismas utilizando una barrena o taladro. Estas propiedades y aplicaciones son bien conocidas en el ramo.

La voladura perimetral es también ampliamente conocida en el oficio. Se trata de un método de control del perímetro de excavación en terreno rocoso, e incluye varias técnicas de voladura usadas habitualmente en aplicaciones de minería y de construcción. Su propósito es controlar y reducir a un mínimo las roturas excesivas en las superficies finales de una excavación en roca. Las técnicas de voladura perimetral incluyen prefracturado, voladuras de superficie uniforme, perforaciones alineadas, voladuras de contorno, voladuras de amortiguación, voladuras de control del plano de fractura, voladuras con capa de aire y otras más. El prefracturado, por ejemplo, es una técnica para superficies que consiste en perforar agujeros paralelos en el plano de la superficie final que se desea lograr en la roca, y detonarlos con cargas ligeras. Esto se hace para generar paredes estables de roca, en lugar de superficies ásperas, desgarradas, inestables y excesivamente atacadas. El objetivo del prefracturado es cargar las perforaciones de manera tal que, para un determinado tipo de roca y un espaciado adecuado, la presión de la perforación al detonar fractura la roca sin exceder su resistencia dinámica a la compresión, evitando así que se triture la roca alrededor de la perforación. Las perforaciones prefracturadas cargadas se detonan antes de que llegue a ellas la onda de impacto principal producida por el estallido central. La estabilidad mecánica resultante en la superficie de la piedra permite obtener pendientes de inclinación y altura mayores, reduce en el largo plazo los costos de mantenimiento de las superficies detonadas, genera condiciones de trabajo más segura para los operarios excavadores y detonadores, reduce al mínimo los costos de definición de la pendiente final y terminación de la superficie, reduce al mínimo la cantidad de terreno requerida para las operaciones de voladura y resulta estéticamente más aceptable.

En las voladuras de superficie uniforme, la superficie rocosa a preservar se halla en superficies elevadas horizontales o aproximadamente horizontales, tales como en la sección del arco de un túnel. Al igual que en el prefracturado, las variables de voladura son el diámetros, la carga y el espaciado de las perforaciones, y las cargas independientes. Las relaciones de carga y espaciado de las perforaciones y sus presiones están destinadas a

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provocar una fractura de agujero a agujero, pero se las mantiene por debajo del umbral de daño en la roca por fallas a la compresión. Los beneficios de la voladura de superficie uniforme son similares a los del prefracturado.

Hay varias maneras de lograr cargas ligeras o tensiones reducidas en las perforaciones perimetrales. Por lo general se usan explosivos empacados con un diámetro de carga apreciablemente menor (la mitad o menos) que el diámetro de la perforación, de modo que la carga no queda adherida al agujero (está desacoplada). También se han usado productos a granel de baja densidad y velocidad reducida, tales como ANFO (nitrato de amonio con aceite combustible) con glóbulos de poliestireno, para lograr un efecto de desacoplamiento y energía reducida; estos productos pueden ser conectados en cadena. Otras alternativas son las cargas de fondo o con capa de aire, en las que las cargas de los productos se colocan solamente en el fondo de las perforaciones, o el espaciado, donde las cargas se colocan en capas separadas para producir una columna explosiva discontinua. Sin embargo, el desacoplamiento resulta menos efectivo en las perforaciones llenas de agua.

Las técnicas de voladura perimetral arriba mencionadas requieren el empleo de diferentes productos o distintos métodos de carga entre las perforaciones perimetrales y los agujeros de la carga principal. Esto aumenta el costo y la complejidad del proceso de voladura. Por el contrario, la presente invención permite usar el mismo producto y básicamente el mismo método de carga en ambos tipos de perforaciones. El agente detonante emulsionado que se usa para la carga principal, o por lo menos el componente emulsificante del agente detonante, es el mismo que se utiliza para las perforaciones perimetrales, con la única diferencia de que se agrega un agente reductor de energía al agente detonante emulsionado, mezclándolo en su totalidad con la emulsión mientras dicha emulsión se introduce en los agujeros perimetrales. De esta manera se coloca una carga de menor energía y menor velocidad en la perforación perimetral, pero esta carga tiene el mismo origen que la carga básica usada para la voladura principal. Es más, puede variarse el nivel de energía entre diferentes perforaciones o aún a lo largo del eje de una misma perforación según se necesite, mediante el aumento o la disminución variable de la cantidad de agente reductor de energía que se agregue.

capítulo reivindicatorio ya que la composición del agente detonante emulsionado no es relevante en la selección del agente reductor de energía. No obstante, hemos replanteado las reivindicaciones pertinentes, lo cual hace el método más claro para el señor examinador.

- Dice el señor examinador que no es claro cuando se habla del paso de "impulsión del agente detonante emulsionado". Agrega el señor examinador que el técnico medio se cuestiona inmediatamente a que se refiere esa impulsión.

En el nuevo capítulo reivindicatorio adjunto se corrige el término "impulsión" por "transportar" que obedece a una traducción más correcta y apropiada del término empleado en el documento original en inglés. Con esto en mente, remitimos al señor examinador al tercer párrafo de la página 8 de la descripción adjunta en la que se define el significado del término "transportado", la cual también aplica al término "transportar". Por lo tanto, el técnico medio no tendría que cuestionarse nada respecto a este paso como se describe en el capítulo reivindicatorio corregido adjunto.

- Dice además el señor examinador que tampoco se entiende como se hace para hacer la mezcla mientras se esta impulsando, y mucho menos como se hace para que quede en forma uniforme y homogénea.

Como se dijo arriba, y como lo sabe el técnico medio en la materia, las características físicas del agente detonante emulsionado, en otras palabras el contenido de gránulos y microesferas de vidrio, hacen que este se comporte como un lecho fluidizado donde las partículas suspendidas ayudan a incrementar la turbulencia dentro de la línea de transporte, con lo cual se logra una mezcla uniforme y homogénea del

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agente detonante emulsionado y el agente reductor de energía.

En cuanto a los requisitos de patentabilidad, el señor examinador objeta la novedad y la altura inventiva de la presente solicitud en vista de lo que divulgan las anterioridades US 6113715 (D1) y US 4474628 (D2). Al respecto se hacen los siguientes comentarios:

- El objeto de la invención de la presente solicitud es el de proporcionar una mezcla explosiva a la que se le añade un agente reductor de la energía con el fin de controlar la potencia de la explosión al momento de la detonación. Para tal fin, el agente reductor de la energía es agua o una solución acuosa. El proceso consiste en tomar un agente explosivo en emulsión que ha sido preparado de antemano, agregarle aditivos sensibilizadores y agregarle agua o una solución acuosa como agente reductor de la energía.
- D1 enseña la formulación de emulsiones explosivas a las que se les adicionan microesféras orgánicas que se expanden por calor para reducir su densidad. Esta reducción de la densidad tiene como objeto aumentar la sensibilidad de la emulsión para que pueda ser utilizada con un detonador convencional.

Dicha anterioridad no enseña o sugiere el uso de un agente reductor de la energía de la emulsión explosiva, menos aun la posibilidad de utilizar agua o las soluciones acuosas divulgadas por la presente solicitud como agentes reductores de energía para el fin que enseña la presente solicitud. Por lo anterior, la presente solicitud es novedosa por sobre lo divulgado en D1.

- D2 enseña una formulación explosiva a la que se adicionan esferas

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Otra ventaja del método de la presente invención reside en que la energía del agente detonante emulsionado puede controlarse en forma variable a lo largo del eje de la perforación, desde abajo hacia arriba en un agujero vertical o desde atrás hacia delante en una perforación horizontal, a medida que se carga en ellos el agente detonante. Esto puede lograrse no sólo variando la cantidad del agente reductor de energía que se agrega, sino también agregando a la emulsión cantidades variables de agentes gasificantes para reducir su densidad también en forma variable. Al combinarse estos factores, la densidad, la sensibilidad y la energía del agente detonante emulsionado pueden ajustarse y modificarse entre distintas perforaciones o aun dentro de un mismo agujero. Estos ajustes permiten compensar las variaciones en la composición de la roca a lo largo de la perforación, aumentando los puntos de presión junto con la profundidad del agujero y otros factores.

Anteriormente se ha agregado agua a los agentes detonantes emulsionado, pero con diferentes propósitos, en diferentes cantidades y/o mediante método diferentes. El agua o la solución acuosa añadida al agente detonante emulsionado en la presente invención se agrega a dicho agente en cantidad suficiente para reducir en forma significativa su energía, y se mezcla en forma uniforme y homogénea durante la fase de emulsión. De hecho, al mezclarse le agua o la solución acuosa de esta manera se forma una segunda fase discontinua de gotitas distinta de la producida por la solución de la sal oxidante usada como componente inicial. Esta segunda fase discontinua da al agente detonante emulsionado mayor sensibilidad y estabilidad que si el agua o la solución acuosa se hubieran combinado inicialmente con al solución de la sal inorgánica oxidante, o si no se hubieran mezclado en forma uniforme y homogénea durante la fase de emulsión. Con la inclusión adicional (opcional) de agentes gasificantes puede obtenerse un agente detonante emulsionado en el que tanto la energía como la densidad y la sensibilidad son variables, brindando así las ventajas descritas anteriormente.

RESUMEN

La presente invención se refiere a un método para reducir la energía de un agente detonante emulsionado y a un método mejorado de voladura

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X 23

X 5

perimetral que comprende (a) formar un agente detonante emulsionado; (b) agregar un agente reductor de energía al agente detonante emulsionado; (c) mezclar el agente reductor de energía con el agente detonante emulsionado en forma uniforme y homogénea; (d) agregar opcionalmente agentes de gasificación a la emulsión para reducir su densidad y aumentar su sensibilidad; y (e) cargar el agente detonante emulsionado dentro de una perforación o una perforación perimetral, respectivamente. La presente invención se refiere asimismo a un agente detonante emulsionado de energía reducida, en el cual se agrega por separado un agente reductor de energía que se mezcla en forma uniforme y homogénea con la emulsión en cantidades que van desde aproximadamente un 5% hasta alrededor de un 22,5% en peso del agente detonante emulsionado.

DESCRIPCION DETALLADA

El agente detonante emulsionado de la presente invención, o el usado en el método de la presente invención, está compuesto por una fase continua de combustible orgánico líquido, una fase discontinua de solución de una sal inorgánica oxidante y, en forma opcional, una dispersión de burbujas gaseosas para aumentar la sensibilidad y reducir la densidad del compuesto o de un agente reductor de densidad.

El combustible orgánico inmiscible que forma la fase continua de la composición se halla presente en una cantidad que puede variar entre el 3% hasta alrededor del 12%, y preferiblemente en una cantidad que varia desde alrededor del 4% hasta casi el 8% del peso del compuesto. La cantidad real usada de combustible orgánico puede variar de acuerdo al tipo específico de combustible(s) no mezclable(s) que se utilice(n) y de la presencia de otros combustibles, si los hubiera. Los combustibles orgánicos no mezclables pueden ser de tipo alifático, alicíclico y/o aromático, y pueden ser saturados y/o no saturados, siempre y cuando tengan estado líquido a la temperatura de uso. Entre los combustibles preferidos se encuentran los siguientes: aceite de pino, aceite mineral, ceras, aceites parafínicos, benceno, tolueno, xilenos, mezclas de hidrocarburos líquidos generalmente conocidas como destilados

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de petróleo, tales como la gasolina (nafta), el queroseno y los combustibles par motores diesel, y los aceites vegetales, como por ejemplo: aceite de maíz, aceite de semilla de algodón, aceite de maní y aceite de soja. Los combustibles líquidos de mayor preferencia son el aceite mineral, el aceite combustible No. 2, las ceras de parafina, las ceras microcristalinas y las mezclas de estos productos. También pueden utilizarse compuestos nitrogenados alifáticos y aromáticos, así como hidrocarburos clorados. Pueden usarse asimismo mezclas de cualquiera de los elementos mencionados anteriormente.

Además del combustible líquido orgánico no mezclable se pueden emplear de forma opcional y en cantidades seleccionadas otros combustibles líquidos o sólidos o de ambos tipos. Algunos ejemplos de combustibles sólidos que pueden usarse son partículas de aluminio finamente pulverizado; materiales carbonosos finamente pulverizados, tales como el asfalto de Utah o el carbón de piedra; granos vegetales finamente pulverizados, tales como el trigo y el azufre. Se pueden usar combustibles líquidos mezclables con agua, que también funcionan como diluyentes. Estos combustibles adicionales de tipo sólido y/o líquido pueden agregarse por lo general en cantidades que pueden llegar hasta un 25% del peso del compuesto. Si se desea, puede añadirse a la composición sal oxidante no disuelta junto con cualquier combustible sólido o líquido.

La solución de la sal inorgánica oxidante que forma la fase discontinua del explosivo se compone generalmente de una sal inorgánica oxidante, en una cantidad que puede variar entre alrededor del 45% hasta alrededor del 95% del peso del compuesto completo, y de agua y/o líquidos orgánicos mezclables con agua, en una cantidad entre alrededor de 0% hasta alrededor del 30%. La sal oxidante preferiblemente usada es el nitrato de amonio (AN), pero pueden usarse otras sales en cantidades de hasta alrededor del 50%. Las otras sales oxidantes se seleccionan de entre el grupo formado por los nitratos, cloratos y percloratos de amonio, de álcalis y de metales alcalinos. De entre estas sales, se prefiere usar el nitrato de sodio (SN) (sodium nitrate) y el nitrato de calcio (CN) (Calcium Nitrate). Pueden añadirse en forma sólida

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X²

gránulos de nitrato de amonio (AN) y de nitrato de amonio con aceite combustible (ANFO) como parte de la sal oxidante en la composición final.

El agua se emplea por lo general en cantidades desde alrededor del 3% hasta alrededor del 30% en peso basándose en la composición total. Es^a unas comúnmente en emulsiones en cantidades desde alrededor del 5% hasta alrededor del 20%.

Para formar una emulsión se usan agentes emulsionantes. Entre los emulsionantes típicos se encuentran: ésteres grasos de sorbitán, ésteres glicólicos, oxazolinas substituidas, alquilaminas o sus sales, derivados de estaos compuesto y elementos similares. Recientemente se han encontrado que ciertos emulsionadotes a base de polímeros imparten mayor estabilidad a las emulsiones bajo determinadas condiciones. Por ejemplo, un emulsionador a base de polímeros derivado del tri-hidroxi-metilaminometano y el anhídrido succínico de polisobutenilo ("PIBSA") es notablemente efectivo en combinación con microesferas orgánicas, y es de uso preferencial. Se han encontrado otros derivados del polipropeno y del polibuteno. Preferiblemente el emulsionador a base de polímeros está compuesto de aminas polimerizadas o sus sales, o de un derivado del tipo amina, alcanolamina o poliol proveniente de un polímero olefinico o con agregado de vinilo, ya sea carboxilado o derivado de un anhídrido.

Los agentes químicos gasificantes se agregan al agente detonante emulsionado preferentemente en el momento de bombear la emulsión dentro de una perforación o inmediatamente antes de hacerlo. Por ello, los agentes químicos gasificantes o los componentes reactivos de los mismos se agregan generalmente después que se ha formado la emulsión. La adición se hace de manera tal que la gasificación se produzca después o al tiempo de haberse completado la manipulación de la emulsión, para llevar al mínimo la pérdida, la migración o la coalescencia de las burbujas gaseosas. Los agentes químicos gasificantes son normalmente solubles en la sal inorgánica oxidante o fase discontinua de la emulsión, y reaccionan químicamente en la fase de la sal oxidante bajo niveles apropiados de pH, produciendo una adecuada dispersión de burbujas de gas dentro de la emulsión. Los agentes químicos gasificantes se componen preferiblemente de una solución acuosa de nitrito

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de sodio y un ácido, que puede ser cítrico o acético. Se prefiere agregar un acelerador de gasificación tal como el tiocianato. Cuando el nitrito de sodio y la sal de tiocianato se combinan en la fase de la solución oxidante que tiene un pH de alrededor de 3.5 hasta alrededor de 5.0, comienza la generación de burbujas de gas. La sal de nitrito puede agregarse en cantidades que van desde menos de 0.1% hasta alrededor del 0.6% en peso del compuesto de la emulsión medido en seco, y el tiocianato u otro acelerador se añaden en una cantidad similar ya sea a la fase discontinua de la solución oxidante o a la solución de nitrito. Para lograr una mayor reducción en la densidad pueden agregarse, además de los agentes gasificantes, esferas huecas o partículas de vidrio, plástico o perlita. La formación de burbujas gaseosas reduce la densidad del agente detonante emulsionado, y por lo general aumenta su sensibilidad a la detonación, hecho conocido en la especialidad.

La fase de la emulsión puede formularse de manera convencional. Típicamente, se disuelven primeramente la(s) sal(es) oxidante(s) en el agua a una temperatura elevada, que dependerá de la temperatura de cristalización de la solución salina. La solución acuosa oxidante se agrega entonces a una solución formada por el emulsificante y el combustible orgánico líquido no mezclable, y la mezcla resultante se agita vigorosamente hasta producir una emulsión de la solución acuosa en una fase continua de combustible orgánico líquido.

Los métodos de la presente invención comprenden agregar un agente reductor de energía y preferentemente agentes gasificantes al agente detonante emulsionado mientras es transportado dentro de una perforación. (La frase "mientras es transportado" cubre la adición del agente reductor de energía ya sea corriente arriba o corriente abajo del medio de transporte usado, tal como una bomba para emulsión.) El término "transportado" incluye bombeado, extrusión u otros medios. Para voladuras perimetrales el agente reductor de densidad puede agregarse en cantidad suficiente como para reducir la energía del agente detonante emulsionado hasta un nivel que permita realizar la voladura perimetral obteniendo los resultados previamente descritos. El agente reductor de energía se mezcla en forma uniforme y homogénea con la fase de la emulsión para formar una segunda fase discontinua, preferiblemente mediante un mezclador dinámico, una válvula

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homogeneizadora, un mezclador estático o tobera(s) de rociado. En forma opcional, pero también preferida, se agregan agentes gasificantes al agente detonante emulsionado para reducir su densidad y aumentar su sensibilidad, lo que puede resultar necesario si el agregado del agente reductor de energía redujera de hecho la sensibilidad a la detonación del agente detonante. Los agentes gasificadores pueden agregarse ya sea antes o después del medio de inyección, tal como una bomba para la emulsión. Los agentes gasificadores se agregan en cantidad suficiente para reducir la densidad del agente detonante emulsionado, en un entorno que va desde alrededor de 0.60 g/cc hasta alrededor de 1.30 g/cc.

El agente reductor de energía se seleccionan entre el grupo formado por el agua y las soluciones acuosas. La sustancia disuelta en las soluciones acuosas se selecciona de entre el grupo formado por las sales inorgánicas oxidantes, la urea, los glicoles y los ácidos inorgánicos. Este agente reductor de energía se agrega en una cantidad que va desde alrededor del 5% hasta alrededor del 22.5% en peso del agente detonante emulsionado, preferiblemente en una cantidad desde alrededor del 7.5% hasta alrededor del 20%, y en un entorno óptimo desde alrededor del 7.5% hasta alrededor del 17.5%.

Al controlar en forma variable la cantidad de agente reductor de energía y de agentes gasificantes que se agrega, pueden variarse la energía, la densidad y la sensibilidad del agente detonante emulsionado en la forma que se desee de perforación a perforación, o a lo largo de la longitud de una perforación, para obtener la versatilidad de detonación que se describió anteriormente. Además se gana en simplicidad y economía al comenzar con un único agente detonante emulsionado que puede usarse en todas las perforaciones del patrón de voladura. De esta manera la presente invención brinda un producto final variable partiendo de un único producto inicial, y resulta particularmente adecuada para voladuras perimetrales.

Se ilustra adicionalmente la invención haciendo referencia a los siguientes ejemplos.

Ejemplo 1

Se prepararon cuatro agentes detonantes emulsionados (mezclas 1-4) y se cargaron en tubos de acero calibre 40 de 76 mm (3") de diámetro por 228,5 mm (24") de largo (Tabla 1). Antes de cargar las mezclas 3 y 4 en los tubos, se dispersó en forma homogénea un agente reductor de energía (agua) dentro del agente detonante emulsionado al 10% y al 20%, respectivamente, por peso de la emulsión. Se utilizó un mezclador manual durante aproximadamente un minuto. Se agregaron agentes reductores de densidad (gasificantes) y se mezclaron en forma similar en las mezclas 2, 3 y 4. (La mezcla 1 se usó como línea de base, y por lo tanto no se le añadió ningún agente reductor de energía ni de densidad.) Se permitió que las mezclas gasificadas se asentaran alrededor de una hora antes de detonarlas.

Se tomaron mediciones de energía al detonar las mezclas. Una comparación de los niveles medidos mostró que la energía total se redujo alrededor de un 34% pasando de 718 cal/g (mezcla 1) a 474 cal/g (mezcla 4, que era un agente detonante emulsionado gasificado con un 20% de agente reductor de energía). La reducción correspondiente de energía por unidad de volumen fue de alrededor del 55%, pasando de 869 cal/cc a 389 cal/cc. La proporción de energía de impacto a burbuja cambió desde alrededor de 56/44 con el agente detonante emulsionado estándar (mezcla 1) a alrededor de 40/60 para el agente detonante emulsionado gasificado con un 20% de agente reductor de energía (mezcla 4). Este traspaso de energía de impacto a burbuja es muy deseable en operaciones de voladura donde se requiere un control de las paredes y del perímetro.

El agente detonante emulsionado usado en las mezclas 1-4 tenía la composición mostrada en la Tabla 2 a continuación. Se agregaron agentes gasificadores a las mezclas 2-4 en la proporción de 0.8% según el peso.

Mezcla Número	Densidad (g/cc)	Velocidad (m/s)	Energía Medida			
			Impacto (cal/g)	Burbuja (cal/g)	Total (cal/g)	Energía por volumen (cal/cc)
1	1.21	6400	401	317	718	869
2	0.87	4820	306	359	665	579
3	0.87	3810	235	313	548	477
4	0.82	4015	188	286	474	389

	% en peso
Solución Oxidante ¹	93.4
Solución Combustible ²	6.0
Microesferas Plásticas	0.6

Densidad de Taza en Caliente (g/cc)	1.13 – 1.16
Viscosidad en Caliente (cP) (± 1,000 cP, husillo #6 a 50 rpm)	13,000

Punto de Condensación: 57-59°C
pH: 4.5 - 5.0
Temperatura: 72-75°C

² Solución Combustible:	Emulsificante	Monooleato	Aceite	Aceite
	<u>Polimérico</u>	<u>de Sorbitán</u>	<u>Combustible</u>	<u>Mineral</u>
	20.0	5.0	37.5	37.5

Temperatura: 60°C

Ejemplo 2

Se formó un agente detonante emulsionado con la formulación mostrada en la Tabla 2. El agente detonante emulsionado se bombeó dentro de un recipiente cuya salida estaba conectada a una bomba.

La salida de la bomba estaba equipada con un accesorio inyector de agua capaz de introducir el agente reductor de energía (agua para este ejemplo). Además, la salida de la bomba estaba también equipada con un accesorio destinado a introducir los agentes gasificantes, colocado antes del inyector de agua. (Los agentes gasificantes empelados en este ejemplo eran una mezcla 20/30/50 de nitrito de sodio/tiocianato de sodio/agua y una mezcla 50/50 de agua y ácido cítrico. Ambos agentes se usaron a un nivel de alrededor del 0.4 por ciento según el peso del agente detonante emulsionado.)

La bomba del agente detonante emulsionado y los tanques de suministro a presión del agente reductor de energía y del agente gasificante se hicieron funcionar simultáneamente, y el flujo combinado de los componentes pasó a través de un dispositivo mezclador (tobera de rociado) instalada en el extremo de una manguera de carga de 6,85 mts (20') de largo y 19 mm (3/4") de diámetro interior. De esta manera la emulsión, el agente reductor de energía y los agentes gasificantes se mezclaron en forma uniforme y homogénea.

Este método se usó para formar dos mezclas que tenían alrededor de 9 y 14 por ciento de agente reductor de energía (agua), respectivamente. Las mezclas se cargaron en tubos de cartón abiertos cuyos diámetros iban desde 32 mm (1-1/4") a 76 mm (3") y se permitió una gasificación desde una densidad inicial de 1.42 g/cc hasta densidades finales de alrededor de 0.85, 0.75 y 0.70 g/cc, respectivamente. Las mezclas requirieron desde 20 a 30

minutos para gasificarse completamente. Los resultados de la detonación a 20°C se presentan en la Tabla 3.

Tabla 3

Mezcla Número	Porcentaje de agua	Diámetro (pulg.)	Densidad (g/cc)	Velocidad (pies/s)
1	9.0	1.25		Falla
1	9.0	2.0		8215
1	9.0	2.5	0.85	8010
1	9.0	3.0		9375
2	14.0	2.0		Falla
2	14.0	2.5	0.75	7680
2	14.0	3.0		8460

Ejemplo 3

La Tabla 4 muestra una serie de mezclas que contenían cantidades variables de agua, desde 0 a 20% por peso de la emulsión (con la misma formulación mostrada en la Tabla 2). Los resultados de la detonación en tubos de cartón abiertos mostraron un aumento considerable en el diámetro crítico y el impulsor minino al aumentar el porcentaje de agua añadida. Los resultados de la detonación en los tubos de 2Acero" calibre 40 (cerrados) indicaron que todas las mezclas, excepto la mezcla 8 que tenía un 20% de agua añadida, detonaron en 38mm con velocidades que iban desde 5.4 km/s sin agua hasta 3.6 km/s con un 17.5% de agua.

Si bien la presente invención se ha descrito haciendo referencia a ciertos ejemplos ilustrativos y condiciones preferidas, las personas versadas en la materia verán la posibilidad de diversas modificaciones, y tales modificaciones deberán considerarse dentro del alcance de la invención de acuerdo a lo expresado en los reclamos adjuntos.

Tabla 4

	Mezcla 1	Mezcla 2	Mezcla 3	Mezcla 4	Mezcla 5	Mezcla 6	Mezcla 7	Mezcla 8
Emulsión	99.3	94.3	91.8	89.3	86.8	84.2	81.7	79.2
% de Agua Agregada	0	5.0	7.5	10.0	12.5	15.0	17.5	20.0
Agentes Gasificantes	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Energía Relativa a 0.84 g/cc ¹ (%)	70.1	64.0	61.1	58.2	55.3	52.4	49.5	46.5
Resultados² a 20°C								
Densidad (g/cc)	0.84	0.83	0.82	0.87	0.82	0.83	0.85	0.82
Velocidad (km/s)								
75 mm	3993	3702	4312	3469	3404	2605	2776	Falla
63 mm	3866	3539	3350	3161	3386	2351	Falla	-
50 mm	4057	3489	3215	2960	3159	Falla	-	-
38 mm	3895	3503	2981	Falla	2863	-	-	-
32 mm	4747	3298	2834	Falla	Falla	-	-	-
25 mm	1860	2822	Falla	-	-	-	-	-
75 mm Acero	4765	4951	3691	4083	3842	4475	4051	4219
50 mm Acero	3907	4212	3469	-	3735	3987	3607	Falla
38 mm Acero	5381	4440	3766	3633	3825	3746	3587	-
Refuerzo Mínimo, 75 mm (det/Falla) ³	#8/#6	#12/#8	2 g/#12	6 g/2 g	6 g/2 g	50/18 g	90/50 g	-
Resultados² a 20°C, 2 semanas								
Densidad (g/cc)	0.83	0.82	0.82	0.84	0.85	-	-	-
Velocidad (km/s)								
75 mm	3802	3980	4312	3812	3409	-	-	-
38 mm	-	-	2981	2662	2648	-	-	-
32 mm	4031	-	2834	-	-	-	-	-
25 mm	Falla	-	-	-	-	-	-	-
Refuerzo Mínimo, 75 mm (det/Falla)	#12/#8	#12/#8	6 g/2 g	6 g/2 g	6 g/2 g	-	-	-

¹ Energía relativa de masa comparada a la energía del ANFO, de 880 kcal/kg.

² Resultados de explosión con el producto alojado en tubos de cartón a menos que se indique otra cosa.

³ Los #12, 8 y 6 son fulminantes (grado de fuerza) y 2 g, 6 g etc., se refiere a gramos de pentolite.

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REIVINDICACIONES

1. Un método mejorado de voladura perimetral que comprende los pasos de:
 - a) formar un agente detonante emulsionado;
 - b) adicionar un agente reductor de energía al agente detonante emulsionado;
 - c) mezclar uniforme y homogéneamente el agente reductor de energía con el agente detonante emulsionado;
 - d) opcionalmente, adicionar agentes gasificantes al agente detonante emulsionado para reducir su densidad y aumentar su sensibilidad; y
 - e) cargar el agente detonante emulsionado transportándolo al interior de una perforación perimetral;

caracterizado por:

seleccionar el agente reductor de energía de entre un grupo formado por agua y soluciones acuosas.
2. Un método mejorado de acuerdo con la reivindicación 1, caracterizado porque se agrega un agente reductor de energía en una cantidad que va desde 5% hasta 22,5% del peso del agente detonante emulsionado.
3. Un método mejorado de acuerdo con la reivindicación 1 caracterizado porque el agente reductor de energía se agrega en una cantidad que va desde 7,5% hasta 17,5% del peso del agente detonante emulsionado.
4. Un método mejorado de acuerdo con la reivindicación 1, caracterizado porque las soluciones acuosas contienen sustancias disueltas seleccionadas de entre el grupo formado por las sales inorgánicas oxidantes, la urea, los glicoles y los ácidos inorgánicos.
5. Un método mejorado de acuerdo con la reivindicación 1, caracterizado porque el agente detonante emulsionado contiene además gránulos de nitrato de amonio o de ANFO en una cantidad de hasta un 50% en peso del agente detonante emulsionado.

6. Un método mejorado de acuerdo con las reivindicaciones 2 o 3, caracterizado porque se agregan agentes gasificantes en cantidades suficientes para reducir la densidad de la emulsión detonante a un rango que va desde 0,60 g/cc hasta 1,30 g/cc. ✓
7. Un método de acuerdo con la reivindicación 1, caracterizado porque el agente reductor de energía forma una segunda fase discontinua en el agente detonante emulsionado.
8. Un método de acuerdo con la reivindicación 1, caracterizado porque la emulsión se transporta por bombeo.
9. Un método para reducir la energía de un agente detonante emulsionado mientras se lo carga dentro de una perforación, que comprende los pasos de:
- a) formar un agente detonante emulsionado;
 - b) adicionar un agente reductor de energía al agente detonante emulsionado;
 - c) mezclar uniforme y homogéneamente el agente reductor de energía con el agente detonante emulsionado en una cantidad que va desde 5% hasta 22,5% en peso del agente detonante emulsionado;
 - d) adicionar agentes gasificantes al agente detonante emulsionado para reducir su densidad y aumentar su sensibilidad; y
 - e) cargar el agente detonante emulsionado transportándolo al interior de una perforación; y
- caracterizado porque:
- el agente reductor de energía se selecciona de entre un grupo formado por agua y soluciones acuosas.
10. Un método de acuerdo con la reivindicación 9, caracterizado porque se agrega el agente reductor de energía en una cantidad que va desde 7,5% hasta 17,5% en peso del agente detonante emulsionado.
11. Un método de acuerdo con la reivindicación 9, caracterizado porque las soluciones acuosas contienen sustancias disueltas seleccionadas de entre el

grupo formado por las sales inorgánicas oxidantes, la urea, los glicoles y los ácidos inorgánicos.

12. Un método de acuerdo con las reivindicaciones 9 o 11, caracterizado porque los agentes gasificantes se agregan en cantidades suficientes para reducir la densidad de la emulsión detonante a un rango que va desde 0,60 g/cc hasta 1,30 g/cc.

13. Un método de acuerdo con la reivindicación 9, caracterizado porque la perforación es una perforación perimetral.

14. Un método de acuerdo con la reivindicación 9, caracterizado porque el agente reductor de energía y los agentes gasificadores se agregan en cantidades variables mientras se carga la perforación para impartir diversos niveles de energía y densidad a la emulsión detonante a lo largo de la perforación.

15. Un método de acuerdo con la reivindicación 9, caracterizado porque el agente reductor de energía forma una segunda fase discontinua en el agente detonante emulsionado.

16. Un método de acuerdo con la reivindicación 9, caracterizado porque la emulsión transportada es bombeada.

17. Un agente detonante emulsionado de energía reducida que comprende:

a) una solución acuosa de una sal oxidante inorgánica que produce en forma de gotas una fase discontinua del agente detonante;

b) un combustible orgánico líquido formando una fase continua;

c) un emulsificante de agua en aceite;

d) burbujas de gas finamente dispersadas en el agente detonante emulsionado, y

e) un agente reductor de energía que se agrega por separado al agente detonante y se mezcla en forma uniforme y homogénea en la emulsión detonante, en una cantidad que va desde 5% hasta 22,5% en peso del agente detonante emulsionado; y

caracterizado porque:

el agente reductor de energía se selecciona de entre un grupo formado por agua y soluciones acuosas.

18. Un agente detonante emulsionado de acuerdo con la reivindicación 17, caracterizado porque se le agrega el agente reductor de energía en una cantidad que va desde 7,5% hasta 17,5% en peso del agente detonante emulsionado.

19. Un agente detonante emulsionado de acuerdo con la reivindicación 17, caracterizado porque las soluciones acuosas contienen sustancias disueltas seleccionadas de entre el grupo formado por las sales inorgánicas oxidantes, la urea, los glicoles y los ácidos inorgánicos.

20. Un agente detonante emulsionado de acuerdo con las reivindicaciones 17 o 18, caracterizado porque se encuentran presentes burbujas de gas en cantidad suficiente para reducir la densidad de la emulsión detonante colocándola en un rango que va desde 0,60 g/cc hasta 1,30 g/cc.

21. Un agente detonante emulsionado de acuerdo con la reivindicación 17, caracterizado porque el agente reductor de energía forma una segunda fase discontinua en el agente detonante emulsionado.

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

2020

Bogotá, D. C., 8 de mayo de 2006

Doctor

JUAN PABLO CADENA SARMIENTORepresentante **DYNO NOBEL INC.****ASUNTO**

Radicación No.	02-42848
Trámite	002
Evento	001
Actuación	430
Oficio	5507
Folios	015

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:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 129 a 142 de la solicitud en estudio. Se aceptan las modificaciones realizadas por el solicitante a este capítulo ya que no implican ampliación de la solicitud inicial.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 21 reivindicaciones en los folios 143 a 146 de la solicitud en estudio. Se aceptan las modificaciones realizadas por el solicitante a este capítulo ya que no implican ampliación de la solicitud inicial, conforme lo establece el artículo 34 de la Decisión 486.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 20 de mayo de 2002, y en el momento de la radicación **SI** se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 09/864339

2) Objeto de la invención

- a) Las reivindicaciones 1 a 24 de la solicitud en estudio se refieren a:
 - i) (1.-) Un método mejorado de voladura perimetral que comprende los pasos de: a) formar un agente detonante emulsionado; b) adicionar un agente reductor de energía al agente detonante emulsionado; c) mezclar uniforme y homogéneamente el agente reductor de energía con el agente detonante emulsionado; e) opcionalmente, adición de agentes gasificantes al agente detonante emulsionado para reducir su densidad y aumentar su sensibilidad; y f) cargar el agente detonante emulsionado transportándolo al interior de una perforación perimetral, caracterizado por seleccionar el agente reductor de energía de entre un grupo formado por agua y soluciones acuosas.

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ii) (9.-) Un método para reducir la energía de un agente detonante emulsionado ...

iii) (17.-) Un agente detonante emulsionado de energía reducida que comprende:...

b) El anterior producto y los procedimientos de obtención buscan mejorar el control de ciertos explosivos.

c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 06 B 25/00

3) Claridad de la Solicitud

a) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro, toda vez que existe una aparente contradicción en lo referido por el solicitante en su respuesta al concepto 1758, en la descripción y en las reivindicaciones.

El solicitante en el folio 127 dice "... lo que el arte no conoce es el uso de agua o soluciones acuosas con el fin de controlar la energía explosiva de una emulsión detonante..." y agrega "...como es bien sabido en el arte, la adición de agua reduce la concentración de los agentes explosivos como el combustible o el nitrato de amonio..." y concluye en este punto "...la presente solicitud enseña una formulación explosiva a la que se le ha reducido la energía y que, así mismo, conserva su sensibilidad a los detonantes convencionales..."

En la descripción refiere (folio 129) "...las composiciones detonantes emulsionadas son muy conocidas en este ramo..." y complementa en el folio 132 "...anteriormente se ha agregado agua a los agentes detonantes emulsionado (sic), pero con diferentes propósitos, en diferentes cantidades y/o mediante método (sic) diferentes".

En las reivindicaciones muestra un método de voladura donde lo nuevo es el empleo de agua y soluciones acuosas y donde los pasos los da por conocidos.

De lo anterior;

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- i) En respuesta al concepto técnico se contradice, toda vez que afirma que no es conocido el usar agua con emulsiones ("... lo que el arte no conoce es el uso de agua o soluciones acuosas...") y sin embargo agrega que es conocido por el arte ("...como es bien sabido en el arte, la adición de agua reduce la concentración de los agentes explosivos como el combustible o el nitrato de amonio...")
 - ii) Se contradice la respuesta al concepto, con la descripción ("... lo que el arte no conoce es el uso de agua o soluciones acuosas...") ("...anteriormente se ha agregado agua a los agentes detonantes emulsionado (sic), pero con diferentes propósitos, en diferentes cantidades y/o mediante método (sic) diferentes".)
 - iii) Puede estarse refiriendo a un nuevo uso de algo conocido ("...anteriormente se ha agregado agua a los agentes detonantes emulsionado (sic), pero con diferentes propósitos, en diferentes cantidades y/o mediante método (sic) diferentes".)
 - iv) Según las reivindicaciones lo nuevo es el uso del agua (método de voladura donde lo nuevo es el empleo de agua y soluciones acuosas y donde los pasos los da por conocidos.) ¿Nuevo uso?

El solicitante debe aclarar muy bien la aparente contradicción que existe entre la descripción el concepto técnico y las reivindicaciones.

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 06 B 21/00 y las más cercanas a ellas, se encontró que antes del 25 de mayo de 2001 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con composiciones para conformar explosivos en emulsión.

De acuerdo con o establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	US 6113715	Method for forming an emulsion explosive composition	2000.09.05
D2	US 4474628	Slurry explosive with high strength hollow spheres	1984.10.02
D3	US 4555278	Stable nitrate emulsion explosives and emulsion for use therein	1985.11.26

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad a las reivindicaciones 19 a 24 en la solicitud en estudio, dado que no es posible realizar una correcta evaluación a las restantes reivindicaciones por lo que se comentó en el punto 3.

a) Evaluación de la novedad y el del Nivel Inventivo

El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

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Como lo relacionan D1 y D2 y todos los documentos que citan, las composiciones explosivas en emulsión son ampliamente conocidas. Ahora, D3 plantea una emulsión que puede mezclarse con agua. Ya que lo que plantea como nuevo el solicitante es que una emulsión pueda mezclarse con agua, este documento lo plantea. Como se ve es exactamente la misma formulación que pretende proteger el solicitante.

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 6113715	1-21	Nivel inventivo
D2	US 4474628	1-21	Nivel inventivo
D3	US 4555278	1-21	Novedad
			Nivel inventivo

6) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. 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 por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


DORIS POLO C.
Jefe División de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en la lista, de fecha

25 MAYO 2006

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
745	202003	

United States Patent [19]
Cescon et al.

[11] **Patent Number:** **4,555,278**
[45] **Date of Patent:** **Nov. 26, 1985**

[54] **STABLE NITRATE/EMULSION
EXPLOSIVES AND EMULSION FOR USE
THEREIN**

[75] **Inventors:** **Lawrence A. Cescon, Hagerstown,
Md.; Nolan J. Millet, Jr.,
Hopatcong, N.J.**

[73] **Assignee:** **E. I. Du Pont De Nemours and
Company, Wilmington, Del.**

[21] **Appl. No.:** **696,200**

[22] **Filed:** **Jan. 29, 1985**

Related U.S. Application Data

[63] **Continuation-in-part of Ser. No. 576,602, Feb. 3, 1984,
abandoned, which is a continuation-in-part of Ser. No.
493,916, May 12, 1983, abandoned.**

[51] **Int. Cl.⁴** **C06B 45/02**

[52] **U.S. Cl.** **149/21; 149/2;
149/46; 149/109.6; 149/110; 102/313**

[58] **Field of Search** **149/2, 21, 109.6, 110,
149/46; 102/313**

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,161,551	12/1964	Egly et al.	149/46
4,111,727	9/1978	Clay	149/2
4,181,546	1/1980	Clay	149/21
4,287,010	9/1981	Owen, II	149/2
4,357,184	11/1982	Binet et al.	149/2
4,404,050	9/1983	Yorke et al.	149/85 X
4,420,349	12/1983	Bampfield	149/85 X

FOREIGN PATENT DOCUMENTS

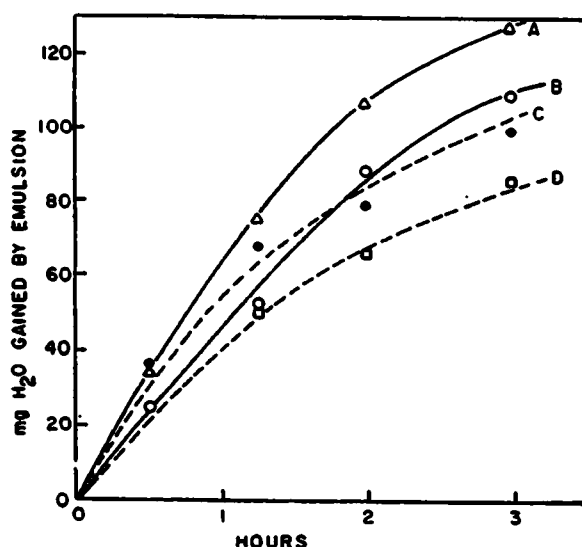
1306546	2/1973	United Kingdom
2004265A	3/1979	United Kingdom
2050340A	1/1981	United Kingdom
2055358A	3/1981	United Kingdom
2125782A	3/1984	United Kingdom

Primary Examiner—Stephen J. Lechert, Jr.
Attorney, Agent, or Firm—Diamond C. Ascani

[57] **ABSTRACT**

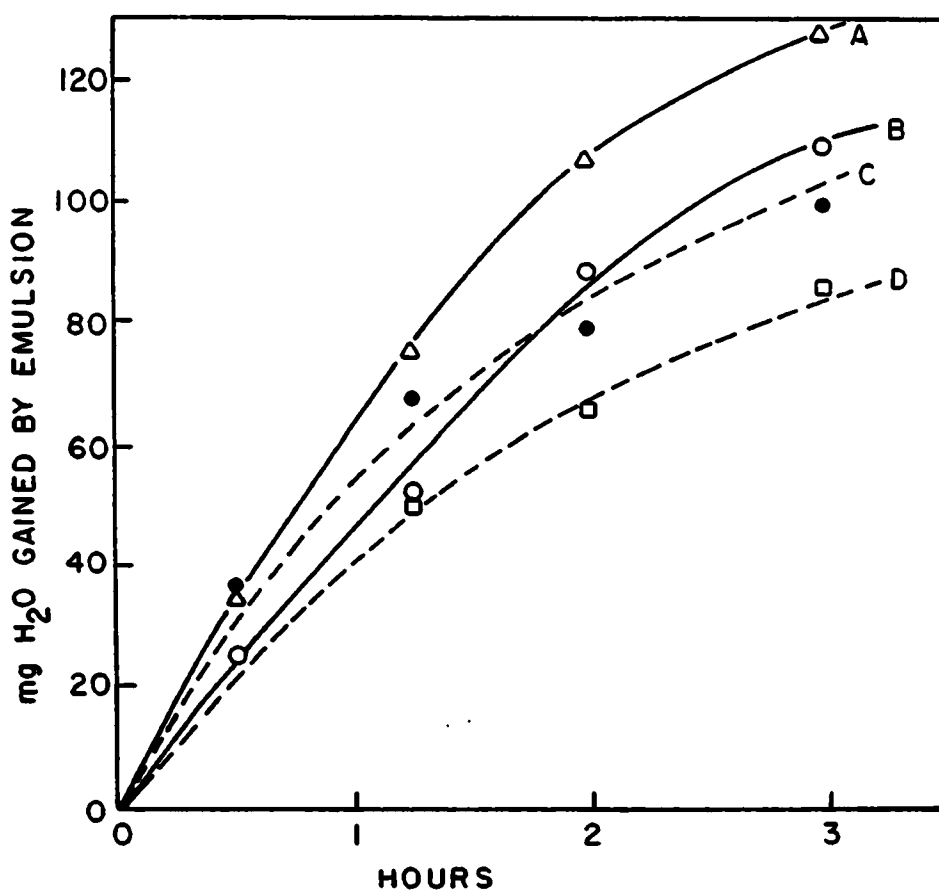
Explosives that are sensitized blends of a water-in-oil emulsion and inorganic nitrate, e.g., AN, particles, such as AN or ANFO prills, have improved stability when their structure hinders the loss of water from the aqueous emulsion phase and transportation of such water across the oil phase to the nitrate particles. Use of an anionic emulsifying agent comprising a fatty acid salt, e.g., as formed in situ during the formation of the emulsion, is the preferred way of forming such a blend-stabilizing structure. Emulsion/nitrate blends stabilized in this manner make satisfactory storage-stable packaged products. Emulsion/nitrate blends made with a new low-viscosity emulsion containing essentially all of the oil required to oxygen-balance the blend and a proportionately larger amount of anionic emulsifying agent to stabilize the emulsion structure constitute preferred bulk products owing to their greater adaptability to pumping. Pumping the stabilized blends through an annular stream of aqueous lubricating liquid is advantageous.

56 Claims, 3 Drawing Figures



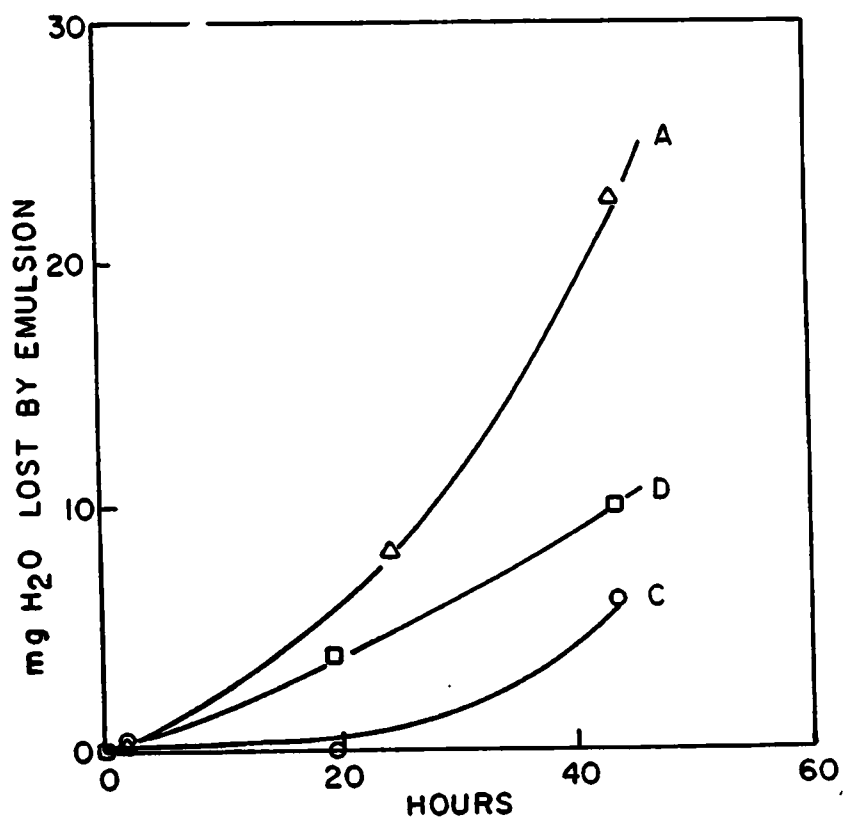
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F I G. 1



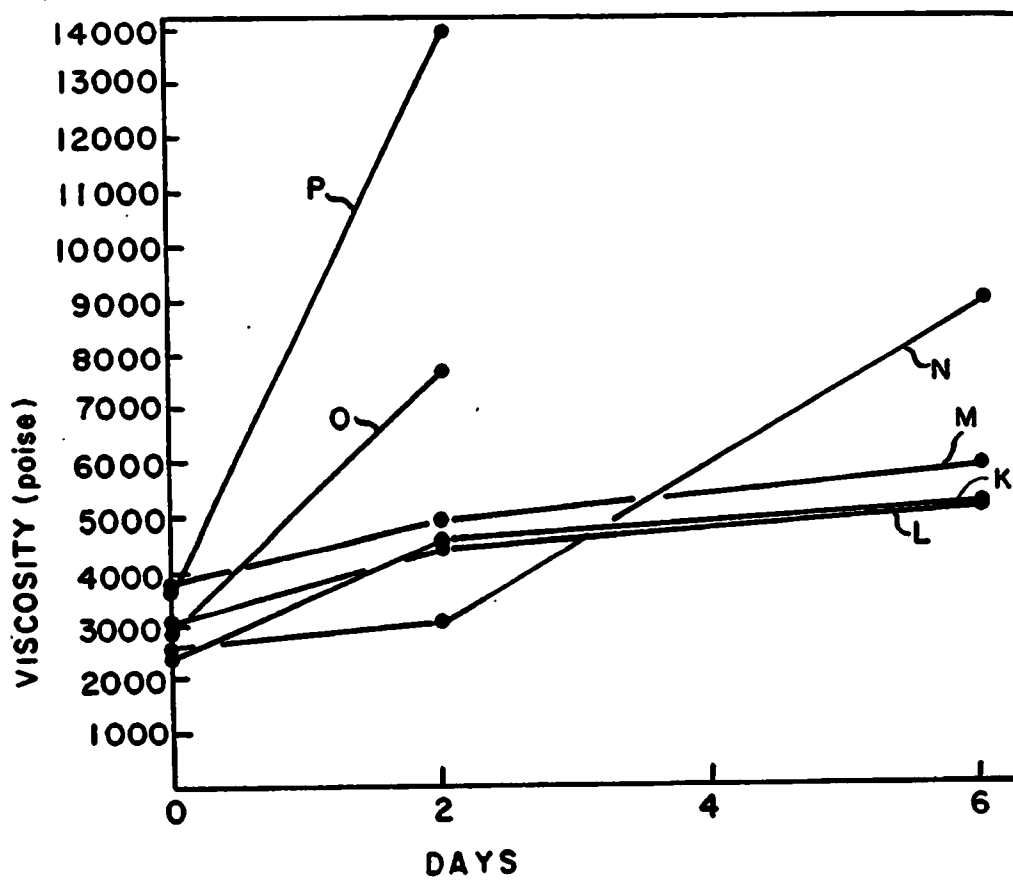
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FIG. 2



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FIG. 3



STABLE NITRATE/EMULSION EXPLOSIVES AND EMULSION FOR USE THEREIN

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of now abandoned application Ser. No. 576,602, filed Feb. 3, 1984, which is a continuation-in-part of now-abandoned application Ser. No. 493,916, filed May 12, 1983.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to explosive compositions comprising a sensitized blend of a water-in-oil emulsion and solid particulate inorganic nitrate, preferably ammonium nitrate (AN), in the form of prills or granules which may be coated with fuel oil (e.g., ANFO), and more particularly to such compositions in the form of storage-stable packaged products and bulk products adapted to be pumped into boreholes. The invention also relates to a low-viscosity emulsion particularly adapted to be blended with fuel-free or -deficient solid inorganic nitrate to form such a blend.

2. Description of the Prior Art

Explosives which comprise a blend of a water-in-oil emulsion and solid particulate AN (e.g., ANFO) have captured the interest of blasters in recent years owing to the fact that they are able to offer the advantages of high bulk density, blasting energy, and water resistance characteristic of emulsion explosives, while at the same time resulting in cost reductions owing to the lower cost of the AN. Among the problems that may be encountered in connection with the use of these blends, however, are those of blend pumpability and blend stability, more particularly of the stability of the blend's explosive properties. Some blends are not pumpable, or only difficultly pumpable. Some must be pumped immediately after they have been formed because they do not retain their pumpability even for a day or two. While there is no question but that the blend must have a sufficiently long shelf life as to be detonable after it has been emplaced in a borehole, this matter has not been dealt with to any significant degree in most of the prior art sources on emulsion/AN blends. Nevertheless, it is a fact that not all packaged blends are detonable by the time they are to be used, even if the packages have been stored for only a short time.

Emulsion/AN blends are described in U.S. Pat. Nos. 3,161,551 (Egly et al.); 4,111,727 (Clay); 4,181,546 (Clay); and 4,357,184 (Binet et al.), and British Pat. No. 1,306,546 (Butterworth). Egly et al. describe an emulsion/AN blend wherein the emulsion, said to be in a sensitized form, is employed as a sensitizer for the solid ammonium nitrate. Regarding the delivery of the blend into a borehole, the patentees describe forming the blend in the borehole itself, i.e., by dropping the AN into the hole and pouring the sensitized emulsion over it.

Clay, whose 10/90 to 40/60 emulsion/AN blends in U.S. Pat. No. 4,111,727 are sensitized only by the air entrapped in the AN, states that the emulsion and AN particles are combined by very simple procedures, preferably just prior to insertion into the borehole. Clay also states that sorbitan monooleate, sorbitan monostearate, and sorbitan monopalmitate are quite suitable emulsifiers for making his emulsion, and that the emulsifiers preferably are blended into the oil before the aqueous

component is added. Clay's AN may be oxygen-balanced ANFO (to be blended with an oxygen-balanced emulsion), or fuel-deficient or fuel-free solid AN (to be blended with an emulsion that contains most or all of the oil required to oxygen-balance the blend).

In U.S. Pat. No. 4,181,546, Clay describes 40/60 to 60/40 emulsion/AN blends having completely filled interstices in and between the AN particles. This product is said to contain too high a proportion of dry ingredient to be pumpable in conventional slurry pumps, but is said to be deliverable to a borehole by an auger in the same manner as dry ANFO. This patent advises minimizing the amount of emulsifier, and using high shear mixing, to insure a stable emulsion. Clay describes sorbitan fatty acid esters as being particularly suitable emulsifiers, and "Glycomul 0" (sorbitan monooleate) as superior to most for his invention.

Butterworth describes loading his blend into an 8.3-cm-diameter polyethylene tube, priming the charge with nitroglycerin, and detonating the charge one hour after mixing. Thus, Egly et al., Clay, and Butterworth do not address themselves to such matters as blend stability, i.e., the condition of the blend after it has been allowed to stand for several days or weeks before or after packaging, or before delivery in bulk form to a borehole.

The emulsion portion of Binet et al.'s explosive composition is termed a "microemulsion", and it contains an amphiphatic synthetic polymer emulsifier, along with a conventional water-in-oil emulsifier. Optionally, a phosphatide emulsion stabilizer is included. Binet et al.'s microemulsion per se, described as a "liqui-liquid foam" of very small cell size ranging from less than 1 micron to about 15 microns, is said to display exceptional long-term storage stability and to be tolerant to doping with further fuel and energy-enhancing ingredients. The patentees discuss a destabilizing seeding crystal effect in prior art emulsion explosives resulting from the presence of solid oxidizer salts in the basic emulsion. According to Binet et al., their findings show that their microemulsion, when doped with 24 percent ground AN, was much more stable to this seeding crystal effect than a prior art emulsion, and remained cap-sensitive for three cycles, each consisting of 3 days of storage at 50° C. followed by 2-3 days at -17° C.

Binet et al.'s consideration of storage stability is directed for the most part at the explosive emulsion itself. The patentees mention that all known prior art water-in-oil emulsions suffer from lack of stability owing to the seeding effect. Binet et al. also imply that the seeding effect is a problem in AN-doped emulsions, although they do not explain how this can be so in microemulsions containing relatively large AN particles. Moreover, Binet et al. require an expensive polymeric emulsifier, and an optional emulsion stabilizer, to achieve improved stability in their microemulsion.

AN/emulsion blends having good storage stability, and a method of making such blends which does not require the use of expensive additives, of perhaps limited utility, are greatly needed to expand the spectrum of AN/emulsion products that can be made available to the public. In particular, blends are needed which are pumpable into a borehole even a few days after having been formed, as well as detonable after having been delivered into a borehole in packaged form after a period of about three months or more from the time the blends were made.

SUMMARY OF THE INVENTION

The present invention provides an improvement in a method of preparing an explosive composition by combining particles of an inorganic nitrate, preferably ammonium nitrate (AN), e.g., AN or ANFO prills, with a water-in-oil emulsion comprising (a) a liquid carbonaceous fuel having components which form a continuous emulsion phase, (b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within the continuous phase, and (c) an emulsifying agent to form a blend of the nitrate particles and the emulsion, which blend contains a sensitizing amount of dispersed gas bubbles or voids. The improvement of the invention comprises forming the nitrate particles and the components of the emulsion into a structure that minimizes the loss of water from the aqueous solution droplets and the transportation of the water across the continuous phase to the nitrate particles mixed with the emulsion. Preferably, this structure includes an emulsion which, when subjected to the following Water Diffusion Test, loses an amount of water that is no more than about 4 percent of the original emulsion weight:

A cylindrical pan of 7.5 mm radius and 2.6 mm height is filled with 0.325 cc of freshly prepared emulsion, which is the same emulsion as that which has been used to prepare the blend. The emulsion's flat exposed surface of 1.25 cm² area is contacted with a cylindrical pellet of an inorganic nitrate having the same cross-sectional area as the emulsion sample and a height of at least 1 cm. The nitrate is the same as that which has been used to prepare the blend. The emulsion/nitrate sample is stored for 48 hours in dry air at 25° C., after which time the emulsion is analyzed for water loss.

In a preferred method of the invention the described structure that hinders water loss and transport is formed by combining the nitrate particles with an emulsion which contains, in its emulsifying system, (a) a salt, preferably an alkali metal, ammonium, and/or alkylammonium salt, of a fatty acid (preferably selected from the group consisting of saturated and mono-, di-, and tri-unsaturated monocarboxylic acids containing about from 12 to 22 carbon atoms), as well as (b) the free fatty acid, the latter being in solution in an oil, the oil solution constituting the continuous emulsion phase, and the fatty acid and fatty acid salt, together with said oil, forming said liquid carbonaceous fuel. Most preferably, the fatty acid salt emulsifying system is one which has been produced in situ from a fatty acid and a base when the oil and the aqueous solution of the inorganic oxidizing salt have been combined to form the emulsion. With this emulsifying system a base, e.g., hydroxide, is present in the emulsion's aqueous phase.

An alternative, or preferably supplemental, way of forming the structure that controls water transport between the aqueous solution droplets and the nitrate particles is to provide a droplet cell size of at least about 1, and preferably no greater than about 4, microns. Still alternatively, or additionally, the structure will be formed by coating the nitrate particles with a substance in which water has a diffusion coefficient at 25° C. of less than about 10⁻⁵ cm²/sec.

Also provided by this invention is a storage-stable packaged explosive product made by one embodiment of the method of the invention and comprising an aged blend of preferably at least about 30 percent by weight of particles of an inorganic nitrate, e.g., ANFO prills,

and preferably at least about 30 percent by weight of an emulsion comprising (a) a liquid carbonaceous fuel including an oil solution of a fatty acid, said solution forming a continuous emulsion phase, (b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within the continuous phase, and (c) an emulsifying system including an emulsifying agent comprising a salt, preferably an alkali metal, ammonium, or alkylammonium salt, of a fatty acid (preferably selected from the group consisting of saturated and mono-, di-, and tri-unsaturated monocarboxylic acids containing about from 12 to 22 carbon atoms), as well as the free fatty acid, the fatty acid and fatty acid salt, together with said oil, forming said liquid carbonaceous fuel, said blend containing a sensitizing amount of dispersed gas bubbles or voids, e.g., an amount which may be at least about 5 percent of the volume of the blend, and whose structure is such that the amount of water lost from the aqueous solution droplets in the emulsion when aged at 25° C. for 2 days is no more than about 4, and preferably no more than about 3.5, percent of the original emulsion weight, as measured by the above-described Water Diffusion Test. In a preferred embodiment, the emulsion has a droplet cell size of at least about 1, and preferably no greater than about 4, microns.

The term "aged" is used herein to distinguish the packaged product of the invention from products which are made at the site of use and delivered into a borehole in bulk form. An "aged" product denotes herein a product which is packaged and transported to the field site at some later date, usually at least several days, and often weeks, after the time of manufacture.

The term "particles of inorganic nitrate" as used herein to describe the solid material that is present in the product of the invention in a blend with an emulsion denotes a solid inorganic oxidizing salt which may be ammonium nitrate, an alkali metal nitrate, e.g., sodium nitrate (SN), or an alkaline-earth metal nitrate, e.g., calcium nitrate (CN), or any combination of two or more of such nitrates, in the form of granules or prills, e.g., fuel-free or fuel-deficient prills, or prills lightly coated with fuel oil, e.g., the well-known "ANFO", in which the usual AN/FO weight ratio is about 94/6, and/or coated according to the method of the invention, as will be described hereinafter. An prills and ANFO are preferred.

In a further embodiment, the present invention provides a water-in-oil emulsion adapted to be blended with inorganic nitrate prills by one embodiment of the method of the invention to form a stable explosive, said emulsion comprising

(a) about from 7 to 21 percent, preferably about from 9 to 15 percent, by weight of a liquid carbonaceous fuel including an oil solution of a fatty acid, said solution forming a continuous emulsion phase;

(b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within the continuous phase; and

(c) an emulsifying system comprising (1) said fatty acid and (2) a fatty acid salt, the oil, fatty acid, and the fatty acid salt together forming the liquid carbonaceous fuel, and the ratio of the amounts of oil and fatty acid added to form the emulsion being in the range of about from 1/1 to 3/1 by weight; said emulsion having an oxygen balance more negative than about -6 percent, e.g., as negative as about -50 percent.

In a preferred emulsion, in which the emulsifying system is one which has been produced in situ from the fatty acid and a base when the oil and the aqueous salt solution have been combined to form the emulsion, a base is also present, as a result of the addition of base and fatty acid in an equivalents ratio of about from 0.5/1 to 3/1, preferably about from 1.5/1 to 2/1. In the above-specified oil to fatty acid ratio in this particular emulsion, the fatty acid weight should be understood to be the weight of fatty acid added to form the emulsion. Some of this becomes converted to the fatty acid salt emulsifier. This emulsion has a viscosity generally in the range of about from 500 to 10,000 poise, and about from 500 to 3,000 poise from bulk products. The emulsion structure is stable for a period of about 3 months or more.

In the emulsion product made by adding a pre-formed fatty acid salt to the system, the "fatty acid" weight in the above-specified oil to fatty acid ratio should be understood to be the weight of fatty acid added plus the weight of fatty acid salt added when the emulsion is being made. In this product the ratio of the weight of fatty acid salt (added) to the weight of fatty acid (added) is at least about 0.5/1.

The amount of inorganic oxidizing salt (the oxidizer) present in the "high oil" emulsion of the invention is insufficient for the complete combustion of the fuel therein, as is evidenced by the emulsion's negative oxygen balance. This oxidizer-deficient emulsion is converted into a product having a more positive oxygen balance and satisfactory explosive properties by blending with fuel-deficient or, preferably, substantially fuel-free inorganic nitrate, preferably AN, prills. By virtue of its relatively low viscosity, the oxidizer-deficient emulsion can be blended with these prills with low shear so as to produce a preferred explosive emulsion/nitrate blend of the invention containing about from 20 to 70 percent by weight of prills and a sensitizing amount of dispersed gas bubbles or voids, the blend being essentially oxygen-balanced, i.e., having an oxygen balance more positive than about -25 percent, and preferably in the range of about from -10 to +5 percent. Blends made from the preferred in situ emulsion and about from 20 to 50 percent prills have a viscosity in the range of about from 2500 to 20,000 poise, a viscosity in this range being maintainable for a period of several days.

BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing, which consists of plots of data obtained in the experiments described in Examples 1, 2, and 7:

FIG. 1 is a plot of the rate at which water is transported into an emulsion used in a product of this invention, as contrasted to an emulsion used in a product of the prior art;

FIG. 2 is a plot of the rate at which water is transported into solid ammonium nitrate from an emulsion used in a product of the invention, as contrasted to an emulsion used in a product of the prior art; and

FIG. 3 is a plot of the viscosities of three blends of the invention and three control blends versus time.

DETAILED DESCRIPTION

The present invention is based on the discovery that the transport of water from the dispersed aqueous phase of the emulsion to the nitrate particles that are intermixed with the emulsion in nitrate/emulsion blends

plays a major role in the instability of these blends, leading to a deterioration of product performance. This transfer of water results in an increase in the water content of the particulate nitrate, perhaps to a level of about 5 to 10 percent, and an increase in the salt concentration in the dispersed aqueous phase, approaching the saturation limit and the possibility that the salt may crystallize out. These combined effects can cause the structure of the emulsion/nitrate blend to deteriorate rapidly.

In the method of the invention, the inorganic nitrate particles and the components of the emulsion, by virtue of their chemical composition and physical properties (e.g., size and spatial relationships), are formed into a structure in the emulsion/nitrate blend that minimizes the loss of water from the droplets of aqueous salt solution, and transportation of the water across the emulsion's continuous phase to the inorganic nitrate particles. This structure provides a medium or barrier resistive to water-transport formed preferably by a substantially hydrophobic continuous emulsion phase, most preferably obtained when the emulsifying system contains a salt, preferably an alkali metal, ammonium, and/or alkylammonium salt, of a fatty acid (e.g., a saturated or mono-, di-, or tri-unsaturated monocarboxylic acid containing about from 12 to 22 carbon atoms), as well as the free fatty acid in solution in an oil, the oil solution of the acid forming the emulsion's continuous phase, and the oil, fatty acid, and fatty acid salt together forming the liquid carbonaceous fuel. Most preferably, this emulsifying system is formed in situ by combining the oil and the aqueous solution in the presence of a fatty acid and a base, according to the method described in U.S. Pat. No. 4,287,010 (Owen). It has been suggested that the Owen in situ method may allow the fatty acid salt (soap) emulsifying agent to form at the oil/water interface, where it is present together with free fatty acid, whereby a stabilizing equilibrium is believed to be established between the acid/soap at the interface, fatty acid in the oil phase, and base in the aqueous phase.

In a most preferred embodiment of the method of the invention, therefore, the emulsifying system is one which has been produced by the in situ formation of a salt, preferably an alkali metal, ammonium, or alkylammonium salt, of a fatty acid (preferably a saturated or mono-, di-, or tri-unsaturated monocarboxylic acid containing about from 12 to 22 carbon atoms), most preferably sodium, potassium, and/or ammonium oleate, according to techniques described in the aforementioned Owen patent.

The importance (to the stability of emulsion/nitrate blends) of a blend structure provided by an emulsion containing a hydrophobic continuous emulsion phase, and more particularly a relatively nonpolar emulsifying system that produces such a continuous phase, has not heretofore been recognized. In fact, Clay (U.S. Pat. No. 4,181,546) says that he found the (non-ionic) sorbitan oleate type to be among the most satisfactory emulsifiers. Binet et al. suggest that stability is dependent on the presence of a graft, block, or branch polymeric emulsifier in combination with conventional emulsifiers. High concentrations of the polar non-ionic emulsifiers in the oil layer render it relatively hydrophilic and therefore capable of transporting water to the inorganic nitrate particles at a rapid rate, leading to the product instability described above. The benefit of the hydrophobic oil layer, as contrasted to the more hydrophilic oil layer

preferred by Clay, is shown in Examples 1 and 2 which follow.

The above-described control of the emulsifying system is the preferred way of providing a structure wherein a hydrophobic medium is present between the aqueous droplets in the emulsion and the inorganic nitrate particles. An alternative method, useful with any emulsifying system but preferably in conjunction with the preferred emulsifying system described above, is to coat the nitrate particles with a substance in which water diffusivity is low, e.g., in which water has a diffusion coefficient at 25° C. of less than about 10^{-5} , and preferably less than about 10^{-8} , cm²/sec. Preferred coating materials are those which, when used in an amount constituting a 6-10 percent of the amount of solid nitrate used, can act as a fuel to oxygen-balance the solid nitrate. Such materials could replace the fuel oil (FO) normally used in ANFO for example. Examples of such materials are solid or semi-solid hydrocarbons including paraffin wax and petrolatum-rosin-paraffin.

In a further preferred embodiment of the invention, the required structure formed by the inorganic nitrate particles and the components of the emulsion is provided by controlling the cell size of the emulsion's internal phase (the aqueous salt solution droplets) so as to decrease the chemical driving force, i.e., the difference between the chemical potential of the water in the dispersed aqueous salt solution of the emulsion and the inorganic nitrate particles. A reduced chemical driving force minimizes the rate of water transport from the aqueous emulsion phase to the nitrate particles. The chemical potential of the components in the dispersed aqueous phase increases in inverse proportion to the radius of curvature of the cell (droplet). Therefore, smaller cell size increases the chemical potential of the water in the discontinuous phase, thereby increasing the driving force for water transport to the solid oxidizer. In the past, a smaller cell size (higher viscosity) has been recommended to increase the stability of emulsion explosives per se. For example, Clay (U.S. Pat. No. 4,181,546) recommends "a good shearing mixing" as well as "a good emulsifier" (sorbitan oleate type) to obtain a good stable emulsion. As is discussed above, the situation is different for emulsion/nitrate blends. The optimum cell size of the internal phase of an emulsion in a blend is the largest that will not crystallize on losing water over the goal shelf life of the product. This insures a minimum rate of water transfer, without premature crystallization of the emulsion. The optimum cell size generally is from about 1 to about 4 microns, decreasing as the aqueous phase water content decreases.

Other factors also can be controlled to minimize water transport across the emulsion's continuous phase. Since the rate of water transport not only is determined by the composition of the continuous phase but also is decreased when the dimensional thickness of this phase is greater, the continuous phase can be made dimensionally thicker by increasing the oil content of the emulsion. Therefore, a preferred product of the invention, especially for use in bulk emulsion/nitrate blends, is a "high oil" emulsion that contains a portion, and preferably substantially all, of the oil required to oxygen-balance the solid inorganic nitrate to be blended therewith. This is beneficial for several reasons. First, the added oil imparts a lower viscosity to the emulsion. Low viscosity is of great benefit in that it permits the formation of

emulsion/nitrate blends with lower shear mixing, which has an advantageous effect on the stability of the blend. Lower shear mixing is especially important in making blends having a high content of solid inorganic nitrate because the movement of the particles past each other during mixing performs work on the emulsion between them which may break the oil film that separates the particles from the aqueous solution droplets, thereby giving water transport a "head start". With the "high oil" emulsion of the invention, and particularly the preferred emulsion in which the emulsifying system is formed in situ, a more stable blend results because the components can be mixed with less shear than that used in blending a more viscous emulsion, and a less viscous, more easily pumpable blend results. Moreover, as will be explained more fully hereinafter, the lower viscosity of the blend is sufficiently stable, at least for several days, so that the advantage of ease of pumping is retained even if a few days elapse between the time when the blend is made and the time when it is pumped.

As has been stated above, increasing the oil content of the emulsion so as to increase the dimensional thickness of the emulsion's continuous phase will increase the resistance to the transport of water across the continuous phase to the inorganic nitrate particles. However, the uncontrolled enlargement of the emulsion's continuous phase often causes the separation or "creaming" of the oil.

It now has been found that in certain specific systems a "high oil" emulsion having an emulsion structure that is stable, i.e., a structure in which there is no "creaming" of the oil phase, can be achieved if the concentration of the emulsifying agent is higher than that used in standard "low oil" emulsions, i.e., essentially oxygen-balanced emulsions which are to be blended with ANFO. If the emulsifying agent is a salt of a fatty acid used in conjunction with the free fatty acid, which is in solution in the oil, and especially if the salt of a fatty acid has been formed in situ as described in U.S. Pat. No. 4,287,010, the stable, low-viscosity emulsion (i.e., the "high oil" emulsion which contains proportionately more emulsifying agent) forms blends with the solid nitrate having a stable viscosity which remains low enough to facilitate pumping even if the blend "ages" a day or so before pumping.

Non-ionic emulsifying agents, such as those of the sorbitan fatty acid ester type, have been stated in the prior art, i.e., in U.S. Pat. No. 4,181,546 (Clay), as having been found to be among the most satisfactory emulsifiers for emulsions, with respect to stability. A new finding, however, is that emulsion/nitrate blends made from "high oil" emulsions containing an emulsifying agent in a concentration that is sufficiently high to preserve the emulsion structure are unstable with respect to viscosity levels when the emulsifying agent is sorbitan monooleate. In the latter case, despite the lower viscosity of the "high oil" emulsion used to form the blend, water transport from the aqueous phase and the possible crystallization of the salt therein can cause the blend viscosity to rise at an extremely rapid rate to a level at which the blend is no longer pumpable and subsequently not detonable. This level may be reached within a day or two. Accordingly, viscosity stability is not a characteristic of "high oil" emulsion/nitrate blends in general, but is dependent upon the nature of the emulsifying system present in the "high oil" emulsion.

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Another benefit of forming blends of the "high oil" emulsion of the invention and oil-free or oil-deficient nitrate prills is that the inclusion of all of the required oil in the emulsion to begin with permits the oil to fatty acid ratio to remain essentially undisturbed in the transition from the unblended to the blended emulsion, hence preserving the required emulsifier level.

Assuming that the preferred "high oil" emulsion of the invention is intended for blending with 20 to 70 percent nitrate prills, the amount of liquid carbonaceous fuel (oil plus fatty acid plus fatty acid salt) present in this emulsion generally will be in the range of about from 7 to 21 percent, based on the total emulsion weight. The amount of liquid carbonaceous fuel in this emulsion is higher as the prill content of the blend in which it is to be used is higher. In the preferred blend range of 40/60 to 60/40 emulsion/prills, the emulsion's liquid fuel content ranges about from 9 to 15 percent by weight, and is no more than about 13 percent in emulsions to be used in bulk products, in which it is beneficial to use no more than about 50 percent prills to facilitate pumping.

The amounts of inorganic oxidizing salt(s) and water present in the aqueous phase of the "high oil" emulsion are within the broad ranges specified for these components in U.S. Pat. No. 4,287,010, i.e., about from 50 to 95 percent oxidizing salt(s) and about from 5 to 25 percent water, by weight. However, within these ranges, higher water concentrations, i.e., about from 12 to 20 percent, are preferred in this emulsion. The content of inorganic oxidizing salt(s), liquid carbonaceous fuel, and water of "low oil" emulsions used in the present method and in the packaged product of the invention will be as described in U.S. Pat. No. 4,287,010.

In the preparation of the emulsifying system according to the in situ method described in the aforementioned U.S. Pat. No. 4,287,010, the disclosure of which is incorporated herein by reference, a fatty acid, e.g., oleic acid, and a base are brought together at the same time as an aqueous solution of an inorganic oxidizing salt and an oil, whereby a fatty acid salt emulsifying agent forms in situ as a water-in-oil emulsion forms. Present in the resulting emulsion is the fatty acid salt, together with the fatty acid (in the oil phase). Base is also present, in the aqueous phase.

The fatty acid salt emulsifying agent used in the preferred embodiment of the present method may be a salt of a saturated or mono-, di-, or tri-unsaturated monocarboxylic acid containing at least about 12, and usually no more than about 22, carbon atoms. Examples of such acids are oleic, linoleic, linolenic, stearic, isostearic, palmitic, myristic, lauric, and brassidic acids. The free fatty acid present may be selected from this same class of monocarboxylic acids. Oleic and stearic acids are preferred on the basis of availability. In "high oil" emulsions to be delivered in bulk form, a fatty acid, e.g., oleic acid, which is liquid at the temperature at which the blend is expected to be used should be selected. Usually, this will be an unsaturated monocarboxylic acid. The cation portion of the fatty acid salt preferably is an alkali metal (e.g., sodium, potassium, or lithium), ammonium, or mono-, di-, or trialkylammonium ion in which the alkyl group(s) preferably contain 1-3 carbon atoms. Sodium, potassium, and ammonium oleates are preferred.

As may be seen from Example 6 which follows, the emulsion structure of the "high oil" emulsion of the invention is many times more stable than a comparable emulsion containing a lower emulsifier concentration.

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To provide the higher emulsifier concentration in the "high oil" emulsion, the weight ratio of oil to fatty acid added to form the emulsion should be in the range of about from 1/1 to 3/1. If pre-formed fatty acid salt is used (i.e., added) to form the emulsion, the weight of "fatty acid" in this ratio should be understood to be the weight of fatty acid added plus the weight of fatty acid salt added, and the ratio of fatty acid salt (added) to fatty acid (added), by weight, should be at least about 0.5/1. The base/acid equivalents ratio used to form the "high oil" emulsion by the in situ method should be in the range of about from 0.5/1 to 3/1, preferably about from 1.5/1 to 2/1.

In the present invention, oils and aqueous inorganic oxidizing salts solutions known to the explosive emulsion art may be employed, preferably those disclosed in the aforementioned U.S. Pat. No. 4,287,010. Most often, the inorganic oxidizing salt present in the emulsion's aqueous phase will be an ammonium, alkali metal, or alkaline earth metal nitrate or perchlorate, preferably ammonium nitrate, alone or in combination with, for example, up to 50 percent sodium nitrate (based on the total weight of inorganic oxidizing salts in the aqueous phase). Salts having monovalent cations are preferred, as explained in U.S. Pat. No. 4,287,010. Suitable oils for use in the liquid carbonaceous fuel include fuel oils and lube oils of heavy aromatic, naphthenic, or paraffinic stock, mineral oil, dewaxed oil, etc.

The "high oil" emulsion of the invention is formed by agitating the aqueous oxidizing salt solution and the oil solution of the fatty acid in the presence of the fatty acid salt under conditions which result in a stable emulsion of a selected viscosity. In the preferred in situ system the base preferably is dissolved in the aqueous solution, which is agitated with the oil solution of the fatty acid.

This emulsion may be blended with nitrate prills (or granules) by pumping it into a mixer or into an auger conveying the nitrate. The latter mode is convenient for making a packaged product. The turning of the screw in the auger blends the emulsion and prills as well as transfers the blend into the package. The low viscosity of the emulsion allows the mixing to be done in a shorter auger length with less shear, resulting in improved shelf life over blends made with high shear.

If the blend of "high oil" emulsion and nitrate prills is to be used in bulk form, e.g., by pumping it from a mixer and into a borehole, perhaps after standing in the mixer for a day or so, the blend remains in a form suitable for pumping after such time owing to its viscosity stability, as is shown in Example 7. The viscosity of a freshly made blend of an emulsion made by the in situ method and containing about from 20 to 50 percent prills generally is in the range of about from 2500 to 20,000 poise, and the blend maintains a viscosity in this range for a period of several days, sufficient to enable pumping to be undertaken during such time.

The inorganic nitrate, preferably AN, with which the "high oil" emulsion is blended is an oil-deficient product, preferably substantially oil-free prills. To produce a blend which is to be pumped, sufficient prills are used to produce a blend having a prill content of from about 20 to 50 percent by weight. Up to 70 percent prills may be used for a packaged product.

The emulsion/prill blend of the invention, whether made with oil-free or oil-containing prills, is in a sensitized form so that it is detonable by means customarily used to initiate explosives. For this reason the blend contains a sensitizing amount of dispersed gas bubbles

or voids (based on blend volume). This void or gas volume can be that of the prills per se (see Examples 5, 6, 9 and 10), or auxiliary gas can be incorporated, e.g., by adding other air-carrying solid materials, for example, phenol-formaldehyde microballoons, glass microballoons, fly ash, etc. If materials of the latter type are to be present in the blend, they may constitute a component of the emulsion or they may be added at the time of blending. With blends containing less than about 50 percent prills and destined to be used to packaged products, it may be desirable to provide an auxiliary source of dispersed gas or voids, such as microballoons, in the blend for the sensitization thereof.

As was mentioned previously, the fatty acid salt emulsifying system is the preferred means of providing the structure that minimizes water loss and transport in the method of the invention. This means is used to best advantage when the fatty acid salt emulsifying system is used in conjunction with high oil content, cell size control, and/or nitrate particle coating, etc. However, in the present method the latter techniques can be used with other emulsifying systems.

The present method is used to advantage in the preparation of blends which contain about from 20 to 70 percent nitrate, preferably AN, particles by weight. The need for a water transport barrier and/or decreased chemical driving force generally is not great with blends containing less than about 20 percent solid nitrate. The solid nitrate content usually will be in the range of about from 30 to 70 percent by weight for a packaged blend, and about from 20 to 50 percent by weight for a pumped blend.

Explosives which are blends of a water-in-oil emulsion and nitrate, preferably AN or ANFO, prills having a physical and chemical structure that minimizes water loss and transport from the emulsion's aqueous phase according to the method of the invention, and especially blends of the "high oil" emulsion of the invention and nitrate prills, are useful in bulk as well as packaged form. The emulsion/nitrate blend of the invention made with the low-viscosity "high oil" emulsion, and particularly the preferred "in situ" emulsion, is especially suited for pumping operations. A preferred technique for pumping the blend into a borehole is to pump it through an annular stream of aqueous lubricating liquid, e.g., naturally occurring water, flowing through the conduit used to transfer the blend to the hole. Such a technique is described in U.S. Pat. No. 4,462,429, issued July 31, 1984, to D. L. Coursen, for pumping a Bingham solid, e.g., a water-in-oil emulsion explosive. By use of a method and apparatus of the type described in the Coursen patent, the disclosure of which is incorporated herein by reference, the resistance of the emulsion/nitrate blend to movement through a conduit is reduced by provision of an annular layer of liquid of low viscosity, e.g., water, around a central column of the blend in the conduit. An annulus of aqueous lubricating liquid, injected into the conduit through which the emulsion/nitrate blend is to be delivered to the borehole, provides lubrication sufficient to permit a column of the blend to slide through the conduit without undergoing appreciable deformation in shear, i.e., movement in "plug flow", a distinct benefit for maintaining the emulsion structure of the blend. An additional benefit of using this apparatus is that it is more effective when used with small amounts of lubricant, which assures better control of the strength and sensitivity of the explosive blend owing to the decreased risk of dilution. A lubricating

liquid flow rate which is no greater than about 5%, and usually no greater than about 0.5-2%, of the emulsion/nitrate blend flow rate is used.

When the pumping is carried out at temperatures above 0° C., water is the preferred lubricating liquid, on the basis of low cost, low viscosity, and immiscibility with the emulsion/nitrate blend being pumped. Additives such as ethylene glycol may be added to the water to reduce its freezing point during cold weather. The water need not be of high purity or even potable. Therefore, any naturally occurring water available at the field site of use can generally be used even though such waters, whether from streams, wells, or the sea, invariably contain some dissolved salts.

The above-described annular lubricant method can be carried out with intermittent pumping, if desired, even in the case in which water is the lubricating liquid. In contrast to the process described in U.S. Pat. No. 4,259,977 for pumping emulsions, in the present process, in which the material being pumped is an emulsion laden with solid nitrate, plugging of the delivery conduit does not occur on stoppage of the pumping operation when a water annulus is used. It is believed that the avoidance of the swelling/plugging problem in the annular lubricant pumping method is related to the nature of the continuous phase in the explosive emulsion used in the present blend, and more particularly to the hydrophobicity thereof resulting from the emulsifying agent or system therein. It is possible that the fatty acid salt, and especially the equilibrium structure of the emulsifying system produced when the emulsifying agent is formed in situ, as is described in the aforementioned U.S. Pat. No. 4,287,010, provide a uniquely hydrophobic environment between the lubricating liquid on the outer surface of the emulsion/nitrate blend and the aqueous phase droplets within the blend, thereby preventing the absorption of the lubricating liquid into the blend despite the presence of a concentration gradient between the lubricating liquid and the aqueous phase droplets. In any event, a matching of such concentrations is unnecessary with the present blends, and any available water supply can be used to provide the lubricating liquid.

The method, emulsion, and emulsion/nitrate blends of the invention will now be described by means of illustrative examples.

EXAMPLE 1

The rate of absorption of water into samples of four different emulsions was measured as an estimate of the relative rates of water transport through these emulsions in emulsion/nitrate blends. The compositions of the samples are shown in the following table. Samples B, C, and D, which are samples of "low oil" emulsions that would be used, for example, in packaged ANFO blends of this invention, were prepared by the method described in Example 1 of U.S. Pat. No. 4,287,010, with variations in mixer speeds as will be described. The percentages given for oleic acid and ammonium hydroxide represent the proportions used to prepare ammonium oleate in situ. Sample A is a sample of an emulsion of the type described in U.S. Pat. No. 3,447,978, in which a non-ionic emulsifying agent is present.

	Sample			
	A	B	C	D
Ammonium Nitrate	75.3	58.9	72.9	72.9

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	Sample			
	A	B	C	D
(dissolved), %				
Sodium Nitrate (dissolved), %	—	13.2	—	—
Water, %	16.3	5.9	15.1	15.1
Oil, %	6.0	3.9	3.9	3.9
Oleic Acid, %	—	2.0	2.0	2.0
Ammonium Hydroxide, %	—	0.5	0.5	0.5
Sorbitan Mono-oleate, %	1.1	—	—	—
Glass Microspheres, %	1.3	—	—	—
Fly Ash, %	—	5.6	5.6	5.6
Mole Fraction of Water in Aqueous Phase	0.49	0.49	0.48	0.48
Density, g/cc	1.25	1.30	1.29	1.29
Relative Cell Size: A < D < C ≈ B				

To test the water absorption rate, the samples were loaded into cylindrical pans of 7.5 mm radius and 2.6 mm height. The samples were submerged under 25.4 mm of water. At various time intervals, a sample was removed, excess water blotted off, and the moisture content measured by Karl Fischer analysis. The results are shown in FIG. 1.

The effect of cell size on the rate of water absorption into the sample is seen by comparing the curves for C and D, which were the same emulsion sheared at different mixer tip speeds to yield different viscosities and cell sizes. The viscosity of C was 1900 poise at 23° C., and the viscosity of D 4550 poise at 23° C., representing the smaller cell size. Because of its smaller cell size, the aqueous phase of D had a higher chemical potential than the aqueous phase of C, resulting in a lower driving force for water transport into the emulsion. After 3 hours, C had gained about 18 percent more water than D.

The effect of the type of emulsifying system on the water absorption rate is more pronounced than the effect of cell size, as can be seen by comparing B, C, or D to A. Although A had the smallest cell size of all the samples (i.e., the least chemical driving force into the emulsion), it gained 49 percent more water than D, apparently because of the poor transport resistance of the continuous phase containing the polar, non-ionic emulsifier.

EXAMPLE 2

The rate of transfer of water from samples of emulsion A, C, and D, described in Example 1, to ammonium nitrate pellets in surface contact therewith was measured as an estimate of the relative rates of transport of water from the emulsion's discontinuous aqueous phase to AN particles in emulsion/AN blends. In this experiment, in which the Water Diffusion Test described previously was performed, the emulsion samples of Example 1 were contacted on the surface with a cylindrical ammonium nitrate pellet of the same cross-sectional area. The water which diffused from the emulsion into the AN pellet is plotted against time in FIG. 2.

A comparison of samples C and D shows that the smaller cells of D increased the driving force for water transport from the emulsion, sample D, after 43 hours, having lost 66 percent more water than sample C. Moreover, water loss was much higher in A than in C or D (losing 283 percent more water than C or D after 43 hours) because of the combined hydrophilicity of the continuous emulsion phase and the higher driving force.

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A high degree of water absorption by the solid AN results in instability of the emulsion/AN blend.

EXAMPLE 3

An emulsion of the following formulation was made by the method described in Example 1 of U.S. Pat. No. 4,287,010:

	%
Ammonium Nitrate (dissolved)	60.8
Sodium Nitrate (dissolved)	13.5
Water	13.7
Oil	3.9
Oleic Acid	2.0
Sodium Hydroxide	0.5
Fly Ash	5.6

The percentages given by oleic acid and sodium hydroxide represent the proportions used to make sodium oleate in situ.

Two blends, A and B, were made with this emulsion:

	Blend A	Blend B
Emulsion, %	50	50
ANFO (94% AN prills	50	—
6% No. 2 Fuel oil), %		
ANWAX (94% AN prills	—	50
6% Paraffin wax), %		

A Differential Scanning Calorimeter (DSC) was used to determine the heat released on crystallization of the unblended emulsion, and of the emulsion component of each blend on cooling at 5° K./min. from 300° K. down to 220° K. These measurements were made when the samples were fresh and after 35 hours of storage at 49° C. Water transport from the emulsion causes concentration of salts in the dispersed aqueous phase and eventual crystallization of the cells. The relative degrees of crystallization present in each sample before cooling can be estimated by measuring the heat released on complete crystallization of the samples by DSC, higher heat release corresponding to less crystallization before cooling. The results were as follows:

Heat Released on Total Crystallization (cal/g)		
Hours at 49° C.	0	35
100% Emulsion	20.5	18.8
Blend A	15.4	8.8
Blend B	17.5	16.2

The above data show that Blend A (the blend with ANFO) was 53% more crystallized than the 100% emulsion sample after 35 hours at 49° C. On the other hand, Blend B (the blend with ANWAX) was only 14% more crystallized, and therefore more stable.

EXAMPLE 4

Emulsion/ANFO blends of various component ratios were prepared by mixing ANFO with an emulsion of the following formulation, prepared as described in Example 1 of U.S. Pat. No. 4,287,010:

Ammonium Nitrate	60.8
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(dissolved), %	
Sodium Nitrate	13.6
(dissolved), %	
Water, %	13.56
Oil, %	3.84
Oleic Acid, %	1.96
Sodium Hydroxide, %	0.54
Microspheres, %	5.7

The stability of the blends after aging was determined by detonating them with or without confinement, and measuring their detonation velocities. The results are shown in the following table:

Emulsion (%)	ANFO (%)	Age at (Days)	Temp. (°C.)	Vel. of Detonation	
				in 12.7 cm diam. (m/sec)	Temp. (°C.)
10	90	163	15	2670*	20
20	80	76	15	4011*	20
25	75	163	15	3250*	20
30	70	163	15	3235*	20
40	60	163	15	2375*	20
50	50	132	15	3950*	20
50	50	101	-7	3890*	5
59	41	40	15	2900**	20
69	31	40	15	2900**	20
79	21	40	15	4800**	20
89	11	40	15	4800**	20

*Confined in steel pipe

**Unconfined

EXAMPLE 5

The following "high oil" emulsions (22.5 kg mixes) were prepared in a 19-liter mixer by adding a 50% aqueous solution of sodium hydroxide to an aqueous solution of ammonium nitrate at 77° C., and adding the base-containing aqueous nitrate solution slowly with agitation to a 30° C. solution of oleic acid in a 3/1, by weight, mixture of No. 2 fuel oil and Gulf Endurance No. 9 oil. The agitator tip speed was 133 cm/sec during ingredient addition, and 400 cm/sec during a subsequent 5-minute shear cycle. The emulsions were then sheared further to reduce the cell size sufficiently to produce a viscosity comparable to that achievable by mixing at 600 cm/sec for an additional 2 minutes.

Emulsion Composition (wt. %)	Emulsion No.				
	A	B	C	D	E
AN	71.4	70.0	68.2	65.3	60.7
water	19.8	19.4	18.9	18.1	16.8
oil	4.6	5.5	6.7	8.6	11.7
oleic acid*	2.7	3.3	4.0	5.1	7.0
NaOH (50% aq. soln)*	1.5	1.8	2.2	2.8	3.8
Oxygen	-9.3	-14.4	-20.9	-31.2	-48.2
Balance					

*Weight added to form oleate emulsifier in situ.

Emulsions A through E (at ambient temperature) were mixed with AN prills to form blends A through E respectively. The mixing was carried out in a cement mixer at medium speed for 4 minutes.

	Blend No.				
	A	B	C	D	E
5 Blend Composition (wt. %)					
Emulsion	70	60	50	40	30
AN Prills	30	40	50	60	70
Oxygen Balance	-0.5	-0.6	-0.5	-0.5	-0.5
Detonation Velocity (m/sec)					
10 in 12.7-cm-diam. steel	3408	—	3401	4130	4188

A typical emulsion which would be blended in the same manner as emulsions A through E above is formulated from the following ingredients:

oil	6.7%
oleic acid	1.3%
sodium oleate	2.7%
Balance:	80% aq. AN solution

EXAMPLE 6

The importance of higher emulsifier levels in "high oil" emulsions was established by preparing the following emulsions in 700-gram quantities by the procedure described in Example 5 except that shearing at 400 cm/sec was performed for only 1 minute. When necessary, the duration of shearing was varied to give emulsion viscosities of 1000 poise. Emulsion stability was measured by centrifuging the emulsion for 10 minutes at 2500 rpm each day for 3 days, at ambient temperature, and determining the weight loss of the continuous (oil) phase.

	Emulsion No.				
	F	G	H	I	J*
40 Emulsion Composition (wt. %)**					
Oil	7.4	7.4	6.7	6.7	8.4
Oleic acid***	3.0	3.0	4.0	4.0	2.0
NaOH (50% aq. soln.)***	1.65	3.3	2.2	4.4	1.1
Oil/acid wt. ratio	2.5	2.5	1.7	1.7	4.2
Base/acid equiv. ratio	1.5	3.0	1.5	3.0	1.5
45 Wt. loss of oil phase (%)	2	1	0	0	27

*Emulsion containing prior art emulsifier level

**Balance 80 weight-% AN solution

***Weight added to form oleate emulsifier in situ

EXAMPLE 7

The stability of the viscosity of blends of AN prills with the "high oil" emulsion of the invention, in contrast to blends made with "high oil" emulsions containing non-ionic emulsifying agents at sufficiently high levels to preserve emulsion stability was demonstrated by measuring the viscosities of six emulsion/prill blends containing 37.6 percent AN prills and 62.4 percent emulsion by weight. Three emulsions (K, L, and M) were according to the invention, and contained different amounts of emulsifying agent all of which were sufficient to produce a stable emulsion. Three emulsions (N, O, and P) were "high oil" control emulsions (i.e., they contained sufficient oil to oxygen-balance the blend with AN prills) that contained a non-ionic emulsifier in three different concentrations, only two of which (in emulsions O and P) were sufficient to prevent "creaming" of the oil phase.

In these emulsions the aqueous phase was a solution which consisted of 69.6% ammonium nitrate, 15.5% sodium nitrate (SN), and 14.9% water by weight. Emulsions K, L, and M were prepared according to the procedure described in Example 7 (with the exception that SN was included in the aqueous phase). Emulsions N, O, and P were prepared by adding sorbitan monooleate to the oil, and the AN/SN solution to the oil solution. Moreover, in the preparation of all six emulsions, exten-

spheres (fly ash) were added during the addition of the AN/SN solution to the oil. Emulsion viscosities were measured with a Brookfield viscometer at 29° C. using a 2 rpm Type E spindle.

The blends were made by mixing the emulsion and AN prills with low shear, by hand with a spatula.

The results are given in the following table, and plotted in FIG. 3.

Emulsion Composition (wt. %)	Emulsion No.					
	K	L	M	N	O	P
AN/SN Solution	81.8	81.8	81.8	82.8	82.8	82.8
Oil	7.5	6.75	5.75	10.9	10.0	8.5
Oleic acid*	4.0	4.75	5.75			
NaOH (50% aq. soln.)*	1.0	1.0	1.0			
Sorbitan mono- oleate (SMO)	—	—	—	0.6	1.5	3.0
Extendspheres	5.7	5.7	5.7	5.7	5.7	5.7
Emulsion viscosity (poise)	575	688	804	529	629	1000

*Weight added to form oleate emulsifier in situ.

Viscosities were measured (as described for the emulsion except at 25° C.) on the freshly made blends as well as on two- and six-day-old blends. Plots of viscosity vs. time for blends K through P are shown in FIG. 3. All blends had initial viscosities in the 2000-4000 poise range. However, while blends of the invention, i.e., blends K, L, and M, showed only a modest viscosity rise over a six-day period, reaching viscosities of only about 4500-5000 poise after six days, the control blends O and P showed a rapid rise within only two days. Control blend N, made from emulsion N, which contained an SMO concentration which was so low as to be insufficient to maintain emulsion stability, exhibited a low rate of viscosity rise over a two-day period, but rose rapidly in viscosity over the next four days. The extremely high viscosities of control blends O and P after two days rendered the blends essentially un pumpable (specifically, unable to flow by gravity from a tank to the suction of a pump), and indicated a deleterious change in the emulsion structure (crystallization in the aqueous phase) which characteristically compromises the blend's ability to detonate. Conversely, blends K, L, and M showed no visual evidence of crystallization and were suitable for pumping.

EXAMPLE 8

The following experiment shows that even stable emulsion/ANFO blends having minimized water transport according to the method of the invention can be improved by the use of the high-oil high-emulsifier emulsion of the invention. Three emulsions, Q, R, and S, were prepared as described in Example 5 for the preparation of emulsions A through E (except that sodium nitrate was included in the aqueous phase in emulsions Q and R, and extenspheres were added in all three, as in Example 7). Emulsions R and S were the

preferred "high oil" emulsions, and emulsion Q was an oxygen-balance emulsion having a lower oil content and emulsifier content than emulsions R and S. Blends R and S were 50/50 emulsion/AN prills. Emulsion Q was blended in the same ratio with ANFO prills, i.e., AN prills lightly coated with fuel oil in a 94/6 AN/oil weight ratio. Blending was carried out in a cement mixer as described in Example 5. The results were as follows:

Emulsion Composition (wt. %)	Emulsion No.		
	Q	R	S
AN	60.8	55.7	67.45
SN	13.6	12.5	—
water	13.0	11.9	14.8
oil	3.85	8.0	7.5
oleic acid*	1.95	4.0	3.0
NaOH (50% aq. soln.)*	1.1	2.2	1.65
Extendspheres	5.7	5.7	5.7

*Weight added to form oleate emulsifier in situ.

Blend Age	Blend No.		
	Q	R	S
13 days	3,097	3,097	3,690
39 days*	1,618	3,306	3,284

*60 days for Blend S

The detonation velocities (m/sec) were measured on 12.7-cm diameter, unconfined samples initiated with a 0.45-kg booster. Although blend Q is comparable to blends R and S at age 39 days in terms of confined detonation velocity, blends R and S do not require confinement at this age (nor does blend S require it at age 60 days) to detonate at acceptable velocities.

EXAMPLE 9

The blends described in Examples 5 and 6 were made with "high oil" emulsions containing no physical sensitizers such as fly ash, glass microballoons, etc. The void or gas volume needed to sensitize these blends was provided by the AN prills used. Five additional blends were made with an emulsion containing no such physical sensitizers, the emulsion used in these blends being a "low oil" (oxygen-balance) emulsion made by the method described in Example 1 of U.S. Pat. No. 4,287,010, except that the sodium nitrate and microspheres were omitted. Its formulation was as follows:

	%
Ammonium nitrate (dissolved)	75.6
Water	17.2
Oil	4.3
Oleic acid*	2.1
NaOH (50% aq. soln.)*	0.6

*Weight added to form oleate emulsifier in situ

This emulsion (at ambient temperature) was mixed with ANFO prills to form blends T, U, V, W, and X. The mixing was carried out in a cement mixer at medium speed for 4 minutes.

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Blend Composition (wt. %)	Blend No.				
	T	U	V	W	X
Emulsion	80	70	60	50	30
ANFO Prills	20	30	40	50	70
Detonation Velocity (m/sec)*					
in 12.7-cm-diam. steel pipe	3409	4646	2843	3432	3810

*Blends T, U tested 2 days after blending
Blend V tested 17 days after blending
Blend W tested 19 days after blending
Blend X tested 20 days after blending

EXAMPLE 10

A "high oil" emulsion of the following formulation was prepared as described in Example 5:

	%
Ammonium nitrate (dissolved)	70.9
Water	16.6
Oil	7.6
Oleic acid*	3.8
NaOH (50% aq. soln.)*	1.1

*Weight added to form oleate emulsifier in situ

The emulsion was blended with sodium nitrate (SN) particles and oil in a weight ratio of 50/46.5/3.5 parts emulsion/SN/oil. This blend detonated after 14 days at a velocity of 4354 m/sec.

EXAMPLE 11

The emulsion described in Example 4 was blended with sodium nitrate particles and oil in various weight ratios, packaged in 12.7-cm diameters, and detonated in 12.7-cm steel pipes with a 0.45-kg primer. The results were as follows:

% Emulsion	% SN	% Oil	Detonation Velocity (m/sec)
88.7	10	1.3	4000 (after 70 days)
76.0	20	4.0	4884 (after 70 days)
64.3	30	5.7	3097 (after 70 days)
52.2	40	7.8	2965 (after 5 days)

What is claimed is:

1. In a method of preparing an explosive composition by combining inorganic nitrate particles with a water-in-oil emulsion comprising (a) a liquid carbonaceous fuel having components which form a continuous emulsion phase, (b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed at discrete droplets within said continuous phase, and (c) an emulsifying agent to form a blend of said particles and said emulsion containing a sensitizing amount of dispersed gas bubbles or voids, the improvement comprising forming said inorganic nitrate particles and the components of said emulsion into a structure that minimizes the loss of water from said droplets and transportation thereof across said continuous oil phase to said nitrate particles.

2. A method of claim 1 wherein said structure is formed by combining said inorganic nitrate particles with an emulsion which contains, in its emulsifying system, a salt of a fatty acid, as well as the free fatty acid in solution in an oil, said oil solution forming said continuous emulsion phase, and said fatty acid, said fatty

acid salt, and said oil together forming said liquid carbonaceous fuel.

3. A method of claim 2 wherein the inorganic nitrate particles combined with said emulsion to form said blend are air-carrying prills, and the emulsion combined with said prills is devoid of a sensitizing amount of dispersed gas bubbles or voids.

4. A method of claim 3 wherein the prills used to form said blend are ANFO prills, and the emulsion used is essentially oxygen-balanced.

5. A method of claim 1 wherein said structure is formed by mixing said particles with an emulsion which has been formed by mixing said liquid carbonaceous fuel and said aqueous salt solution at a rate and for a time sufficient to produce a cell size of said discontinuous emulsion phase in the range of about from 1 to 4 microns.

6. A method of claim 1 wherein said structure is formed by coating said particles with an agent in which water has a diffusion coefficient at 25° C. of less than about 10^{-5} cm²/sec.

7. A method of claim 1 wherein said inorganic nitrate particles are AN prills, ANFO prills, or a combination thereof.

8. A method of claim 1 wherein said blend is formed and thereafter packaged.

9. A method of claim 8 wherein said emulsion, when aged at 25° C. for 2 days, loses no more than about 4 percent of its original weight when subjected to the following Water Diffusion Test: filling a cylindrical pan of 7.5 mm radius and 2.6 mm height with 0.325 cc of freshly prepared emulsion, contacting the emulsion's flat exposed surface of 1.25 cm² area with a cylindrical pellet of an inorganic nitrate having the same cross-sectional area as the emulsion sample and a height of at least 1 cm, and storing the emulsion/nitrate sample for 48 hours in dry air at 25° C., after which time the emulsion is analyzed for water loss.

10. A method of claim 8 wherein said structure is formed by combining said nitrate particles with an emulsion which contains, in its emulsifying system, a salt of a fatty acid, as well as the free fatty acid in solution in an oil, said oil solution forming said continuous emulsion phase, and said fatty acid, said fatty acid salt, and said oil together forming said liquid carbonaceous fuel.

11. A method of claim 10 wherein said fatty acid is selected from the group consisting of saturated and mono-, di-, and tri-unsaturated monocarboxylic acids containing about from 12 to 22 carbon atoms, and said salt is an alkali metal, ammonium, and/or alkylammonium salt.

12. A method of claim 10 wherein said structure is formed by combining said nitrate particles with an emulsion that has been obtained by combining said oil and said aqueous solution with agitation in the presence of said fatty acid and a base so as to form said fatty acid salt emulsifying agent in situ.

13. A method of claim 8 wherein said structure is formed by mixing said particles with an emulsion which has been formed by mixing said liquid carbonaceous fuel and said aqueous salt solution at a rate and for a time sufficient to produce a cell size of said discontinuous emulsion phase in the range of about from 1 to 4 microns.

14. A method of claim 8 wherein said structure is formed by coating said particles with an agent in which

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water has a diffusion coefficient at 25° C. of less than about 10^{-5} cm²/sec.

15. A method of claim 10 wherein said particles constitute at least about 20 percent, and said emulsion constitutes at least about 20 percent, by weight of said blend.

16. A method of claim 10 wherein said inorganic nitrate particles are AN prills, ANFO prills, or a combination thereof.

17. In a method of preparing an explosive composition by combining inorganic nitrate particles with a water-in-oil emulsion comprising (a) a liquid carbonaceous fuel having components which form a continuous emulsion phase, (b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within said continuous phase, and (c) an emulsifying agent to form a blend of said particles and said emulsion containing a sensitizing amount of dispersed gas bubbles or voids, the improvement comprising combining inorganic nitrate prills with an emulsion which contains liquid carbonaceous fuel in an amount sufficient to essentially oxygen-balance said prills and said inorganic oxidizing salt present in said aqueous solution, said emulsion containing, in its emulsifying system, a salt of a fatty acid, as well as the free fatty acid in solution in an oil, said oil solution forming said continuous emulsion phase, and said fatty acid, said fatty acid salt, and said oil together forming said liquid carbonaceous fuel.

18. A method of claim 17 wherein said fatty acid is selected from the group consisting of saturated and mono-, di-, and tri-unsaturated monocarboxylic acids containing about from 12 to 22 carbon atoms, and said salt is an alkali metal, ammonium, and/or alkylammonium salt.

19. A method of claim 18 wherein said structure is formed by combining said nitrate prills with an emulsion that has been obtained by combining said oil and said aqueous solution with agitation in the presence of a fatty acid and a base so as to form a fatty acid salt emulsifying agent in situ.

20. A method of claim 19 wherein the amount of liquid carbonaceous fuel in said emulsion is about from 7 to 21 percent, based on the weight of said emulsion.

21. A method of claim 20 wherein the amounts of fatty acid and base added to form said fatty acid salt in situ are sufficient that the ratio of the amount of oil added to the amount of fatty acid added is in the range of about from 1/1 to 3/1 by weight, and the equivalents ratio of the amount of base added to the amount of fatty acid added is in the range of about from 0.5/1 to 3/1.

22. A method of claim 21 wherein said fatty acid is oleic acid, and said fatty acid salt is ammonium oleate and/or one or more alkali metal salts of oleic acid.

23. A method of claim 17 wherein said blend is formed from an emulsion that is devoid of a sensitizing amount of dispersed gas bubbles or voids.

24. A method of claim 17 wherein supplemental air-carrying solid materials are combined with said prills and emulsion.

25. A method of claim 17 wherein said prills are AN prills.

26. A method of claim 25 wherein said AN prills constitute about from 20 to 70 percent by weight of said blend.

27. A water-in-oil emulsion adapted to be blended with inorganic nitrate prills to form an explosive, said emulsion comprising

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(a) about from 7 to 21 percent by weight of a liquid carbonaceous fuel including an oil solution of a fatty acid, said solution forming a continuous emulsion phase;

(b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within said continuous phase; and

(c) an emulsifying system comprising (1) said fatty acid and (2) a fatty acid salt, said oil, fatty acid, and fatty acid salt together forming said liquid carbonaceous fuel, and the ratio of the amounts of oil and fatty acid added to form said emulsion being in the range of about from 1/1 to 3/1 by weight; said emulsion having an oxygen balance more negative than about -6 percent.

28. An emulsion of claim 27 wherein said emulsifying system is one which forms in situ from a fatty acid and a base as said oil and said aqueous solution are brought together to form said emulsion, the ratio of the amount of base added to the amount of fatty acid added to form said emulsifying system being about from 0.5/1 to 3/1 by weight.

29. An emulsion of claim 28 having a viscosity in the range of about from 500 to 10,000 poise, and stable in emulsion structure for a period of at least about 3 months.

30. An emulsion of claim 27 wherein said emulsifying system is formed by adding a fatty acid and a salt of a fatty acid to the other components of the emulsion, said ratio of oil to "fatty acid" being understood to be the ratio of oil to fatty acid plus fatty acid salt added when the emulsion is being made, and the ratio of said fatty acid salt added to fatty acid added being at least about 0.5/1.

31. An emulsion of claim 27 wherein said fatty acid salt is selected from alkali metal, ammonium, and alkylammonium salts of saturated and mono-, di-, and tri-unsaturated monocarboxylic acids containing about from 13 to 22 carbon atoms.

32. An emulsion of claim 31 wherein said fatty acid is oleic acid, and said fatty acid salt is ammonium oleate and/or one or more alkali metal salts of oleic acid.

33. An emulsion of claim 27 containing dispersed air-carrying inert solid materials.

34. An emulsion of claim 27 devoid of a sensitizing amount of dispersed gas bubbles or voids.

35. An essentially oxygen-balanced water-in-oil emulsion adapted to be blended with inorganic nitrate prills and oil to form an explosive, said emulsion comprising

(a) a liquid carbonaceous fuel including an oil solution of a fatty acid, said solution forming a continuous emulsion phase;

(b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within said continuous phase; and

(c) an emulsifying system comprising (1) said fatty acid and (2) a fatty acid salt, said oil, fatty acid, and fatty acid salt together forming said liquid carbonaceous fuel;

said emulsion being devoid of a sensitizing amount of dispersed gas bubbles or voids.

36. An emulsion of claim 35 wherein said prills and oil with which said emulsion is adapted to be blended are AN prills mixed with fuel oil.

37. An explosive product comprising a blend of about from 30 to 80 percent by weight of the emulsion of

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claim 27 and about from 70 to 20 percent by weight of inorganic nitrate prills sufficient to essentially oxygen balance said emulsion, said blend containing a sensitizing amount of dispersed gas bubbles or voids.

38. An explosive product comprising a blend of about from 50 to 80 percent by weight of the emulsion of claim 28 and about from 50 to 20 percent by weight of ammonium nitrate prills sufficient to essentially oxygen balance said emulsion, said blend containing a sensitizing amount of dispersed gas bubbles or voids, having a viscosity in the range of about from 2500 to 20,000 poise, and remaining in said range for a period of several days.

39. An explosive product of claim 37 wherein said dispersed gas is the gas present in said ammonium nitrate prills.

40. An explosive product of claim 37 wherein supplemental air-carrying solid materials are present.

41. An explosive product of claim 37 wherein the prill content is about from 40 to 60 percent by weight, and the liquid carbonaceous fuel content of said emulsion is about from 9 to 15 percent by weight.

42. A method of delivering the explosive product of claim 38 to a borehole through a conduit comprising pumping said product to the borehole through an annular stream of aqueous lubricating liquid flowing through the conduit in the same direction as the explosive product, said product being adapted to resume flowing when pumping is resumed after extended periods of rest in said conduit, independently of the composition of said aqueous lubricating liquid.

43. A method of claim 42 wherein said aqueous lubricating liquid is naturally occurring water.

44. An aged, storage-stable explosive product comprising, in a package, a blend of particles of ammonium nitrate (AN) and an emulsion comprising (a) a liquid carbonaceous fuel including an oil solution of a fatty acid, said solution forming a continuous emulsion phase, (b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within the continuous phase, and (c) an emulsifying system including an emulsifying agent comprising (1) an alkali metal, ammonium, or alkylammonium salt of a fatty acid containing about from 12 to 22 carbon atoms, as well as (2) the free fatty acid, said fatty acid, said fatty acid salt, and said oil together forming said liquid carbonaceous fuel, and said blend containing dispersed gas bubbles or voids comprising at least about 5 percent of its volume, said emulsion, when aged at 25° C. for 2 days, losing no more than about 4 percent of its original weight when subjected to the following Water Diffusion Test: filling a cylindrical pan of 7.5 mm radius and 2.6 mm height with 0.325 cc of freshly prepared emulsion, contacting the emulsion's flat exposed surface of 1.25 cm² area with a cylindrical pellet of ammonium nitrate having the same cross-sectional area as the emulsion sample and a height of at least 1 cm, and storing the emulsion/AN sample for 48 hours in dry air at 25° C., after which time the emulsion is analyzed for water loss.

45. An explosive product of claim 44 wherein said emulsion has been obtained by combining said aqueous

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solution and an oil with agitation in the presence of a fatty acid and a base so as to form said fatty acid salt in situ, said emulsifying system also containing base.

46. An explosive product of claim 45 wherein said AN particles constitute at least about 20 percent, and said emulsion constitutes at least about 20 percent, of said blend by weight.

47. An explosive product comprising a blend of inorganic nitrate prills and an emulsion comprising (a) a liquid carbonaceous fuel having components which form a continuous emulsion phase, (b) an aqueous solution of an inorganic oxidizing salt forming a discontinuous emulsion phase dispersed as discrete droplets within the continuous phase, and (c) an emulsifying system including an emulsifying agent comprising a salt of a fatty acid, as well as the free fatty acid in solution in an oil, said oil solution forming said continuous emulsion phase, and said fatty acid, said fatty acid salt, and said oil together forming said liquid carbonaceous fuel, said blend containing a sensitizing amount of dispersed gas essentially provided by said prills.

48. An explosive product of claim 47 wherein said prills are AN prills which constitute about from 20 to 80 percent by weight of said blend.

49. An explosive product of claim 48 wherein the ammonium nitrate prills used to form the blend are ANFO prills, and the emulsion used is an essentially oxygen-balanced emulsion.

50. A method of claim 1 wherein a substantially hydrophobic medium is present between said inorganic nitrate particles and the aqueous droplets in said emulsion.

51. A method of claim 1 wherein said emulsion, when aged at 25° C. for 2 days, loses no more than about 4 percent of its original weight when subjected to the following Water Diffusion Test: filling a cylindrical pan of 7.5 mm radius and 2.6 mm height with 0.325 cc of freshly prepared emulsion, contacting the emulsion's flat exposed surface of 1.25 cm² area with a cylindrical pellet of an inorganic nitrate having the same cross-sectional area as the emulsion sample and a height of at least 1 cm, and storing the emulsion/nitrate sample for 48 hours in dry air at 25° C., after which time the emulsion is analyzed for water loss.

52. A method of claim 1 wherein said emulsion constitutes about from 10 to 90 percent, and said particles about from 90 to 10 percent, by weight of said blend.

53. A method of claim 9 wherein said emulsion constitutes about from 10 to 90 percent, and said particles about from 90 to 10 percent, by weight of said blend.

54. A method of claim 17 wherein said emulsion constitutes about from 10 to 90 percent, and said prills about from 90 to 10 percent, by weight of said blend.

55. A method of claim 51 wherein said emulsion constitutes about from 10 to 90 percent, and said particles about from 90 to 10 percent, by weight of said blend.

56. An explosive product of claim 44 wherein said emulsion constitutes about from 10 to 90 percent, and said particles about from 90 to 10 percent, by weight of said blend.

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