

Bogotá, 8 de mayo de 2024

Doctora

Edna Marcela Ramírez Orozco

Directora Nuevas Creaciones

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO -SIC-

E.

S.

D.

REF.: SOLICITANTES : YARA INTERNATIONAL ASA

**TITULO : MÉTODO PARA PRODUCIR UN FERTILIZANTE
QUE CONTIENE POTASIO CON UN BAJO
CONTENIDO DE MATERIAL NO HIDROSOLUBLE**

**No. de Solicitud : PCT/EP2022/078604
Internacional**

**ENTRADA A FASE NACIONAL EN COLOMBIA CON LAS MODIFICACIONES QUE
SE LLEVARON A CABO EN FASE INTERNACIONAL BAJO ARTÍCULO 34
(CAPÍTULO II)**

HELENA CAMARGO WILLIAMSON, mayor de edad y vecina de Bogotá D.C., identificada como aparece al pie de mi firma, en mi condición de apoderada de la sociedad **YARA INTERNATIONAL ASA**, adjunto este memorial con el fin de brindar mayor claridad al Examinador a la hora de revisar los documentos radicados. Así, me permito señalar que la presente solicitud entrara a fase nacional en Colombia con las modificaciones que se llevaron a cabo en fase internacional presentadas en Capítulo II bajo le artículo 34.

Así las cosas, me permito adjuntar la traducción de la solicitud con modificaciones bajo artículo 34 (Capítulo II), el cual comprende las reivindicaciones modificadas, además, de la traducción de la descripción, reivindicaciones y resumen originalmente presentados en fase internacional. Y, por último, adjuntamos algunos de los documentos que se han presentado y emitido durante la fase internacional, tales como la publicación internacional, el reporte de búsqueda y opinión escrita, forma PCT/RO/105, Forma PCT/IB/304, demanda presentada ante la WIPO IPRP (Capítulo II), carta en respuesta al ISR, forma PCT/IPEA/408, carta presentada a la WO2, forma PCT/IPEA/416, entre otros.

De acuerdo con todo lo anterior, amablemente solicitamos que proceda a llevar a cabo el trámite de la solicitud y el estudio de patentabilidad a las reivindicaciones radicadas y basadas en las modificaciones bajo el artículo 34 (capítulo II) de la solicitud internacional. Así las cosas, considero que la presente invención cumple con todos los requisitos formales de acuerdo con el numeral 5.2.5. del Título X de la Circular Única de la Superintendencia y la Decisión 486.

De la Señora directora,

POSSE HERRERA RUIZ



**HELENA CAMARGO WILLIAMSON
C.C 35.455.268 de Bogotá
T.P. 76.985**

MÉTODO PARA PRODUCIR UN FERTILIZANTE QUE CONTIENE POTASIO CON UN BAJO CONTENIDO DE MATERIAL NO HIDROSOLUBLE

DESCRIPCIÓN

5

CAMPO DE LA INVENCION

La presente invención se refiere al campo de producción de fertilizante, en particular, la producción de fertilizantes NPK con un bajo contenido de material no hidrosoluble.

10

ANTECEDENTES DE LA INVENCION

Nitrógeno (N), fósforo (P) y potasio (K) son los tres nutrientes primarios que necesitan la mayoría de los cultivos para crecer. Los suelos contienen naturalmente diversas cantidades de estos nutrientes, pero para alcanzar un crecimiento y rendimiento óptimos, los agricultores generalmente agregan fuentes de estos nutrientes.

15

Además, los cultivos también pueden necesitar nutrientes secundarios (calcio, magnesio y azufre) y micronutrientes (boro, cobre, hierro, molibdeno, manganeso y zinc).

20

Los productos fertilizantes, en particular, los productos fertilizantes sólidos, tales como los globulillos o gránulos, se usan desde hace siglos. El fertilizante sólido puede comprender uno o más nutrientes, y los productos fertilizantes que contienen más de un nutriente tienen la ventaja de que reducen la cantidad de aplicaciones que debe hacer el agricultor al proporcionar varios nutrientes a los cultivos en una única aplicación.

25

Un fertilizante NPK se refiere a un producto que contiene todos nutrientes primarios: N, P y K. Existe de diferentes maneras y se pueden usar diferentes materias primas para producir estos fertilizantes. En general, los fertilizantes NPK se denominan de forma X/Y/Z, en donde X, respectivamente Y, y Z, es el % en peso de N (expresado como nitrógeno), respectivamente P (expresado como P_2O_5), y K (expresado como K_2O).

30

Una característica importante de los fertilizantes sólidos es la cantidad de material no hidrosoluble que contienen. Puede ser ventajoso producir un producto NPK con una cantidad muy baja, tal como menos de 1,0% en peso, de material no hidrosoluble, ya que tal producto puede usarse en fertirrigación, en donde el producto fertilizante se disuelve primero en agua y se distribuye en los cultivos por medio del sistema de irrigación. Este método de fertilización está adquiriendo popularidad e interés

35

ya que reduce el consumo de agua y permite que la aplicación de fertilizante sea muy

precisa. La fertirrigación requiere un producto fertilizante que tenga una baja cantidad de material no hidrosoluble, ya que el material no hidrosoluble puede obstruir las líneas de riego.

5 Sin embargo, los productos fertilizantes con una baja cantidad de material no hidrosoluble, en particular, los productos fertilizantes NPK, no son fáciles de obtener, en particular, donde el método de producción usa sulfato de potasio (SOP) como fuente de potasio.

Existe la necesidad de proporcionar un nuevo método de producción que proporcione un producto fertilizante con una baja cantidad de material no hidrosoluble.

10

BREVE DESCRIPCIÓN DE LA INVENCION

Se descubrió que una fuente importante de material no hidrosoluble en un producto, en particular, un producto fertilizante, que usa SOP como fuente de potasio se encontraba en el SOP, en particular, en donde el SOP se había preparado mediante el proceso Mannheim. En el proceso Mannheim para la producción de SOP, el ácido sulfúrico se hace reaccionar con cloruro de potasio para obtener sulfato de potasio. Esta reacción usa un exceso de ácido sulfúrico para garantizar la conversión total del cloruro de potasio. Sin embargo, si el SOP resultante tiene un pH demasiado bajo, en particular, debajo de $\text{pH} = 3$, las etapas de producción posteriores para obtener un producto fertilizante pueden enfrentarse con problemas, tales como una viscosidad muy alta y/o mayores riesgos de seguridad.

20 Para remediar uno o más de estos problemas, es importante aumentar el pH del SOP hasta al menos 3,5 (medido como 10% en peso de solución acuosa). Para neutralizar el exceso de ácido sulfúrico y aumentar el pH del SOP habitualmente se agrega óxido de calcio. Sin embargo, cuando el óxido de calcio reacciona con ácido sulfúrico, se forma sulfato de calcio y el sulfato de calcio tiene una solubilidad en agua muy baja, y esto aumenta la cantidad de material no hidrosoluble en el SOP y, por lo tanto, en el producto final.

25 Se descubrió que es posible reemplazar el óxido de calcio usado para neutralizar el ácido sulfúrico con otro compuesto, a saber, óxido de magnesio. El óxido de magnesio también puede reaccionar con ácido sulfúrico y aumenta el pH del SOP. Una ventaja de usar óxido de magnesio es que este se convierte en sulfato de magnesio durante la etapa de neutralización. El sulfato de magnesio tiene una muy buena hidrosolubilidad y no aumenta el contenido de material no hidrosoluble del producto final.

En un primer aspecto, la presente divulgación proporciona un método para producir una composición particulada sólida que comprende de 0 a 2,0% en peso de material no hidrosoluble, en donde el método comprende las etapas de: a) mezclar cloruro de potasio y ácido sulfúrico, y producir así una composición que comprende sulfato de potasio y ácido sulfúrico; b) agregar óxido de magnesio a la composición obtenida en la etapa a), y neutralizar así el ácido sulfúrico comprendido en la composición obtenida en la etapa a); c) agregar la composición obtenida en la etapa b) a una composición que comprende nitrógeno (N) y/o fósforo (P); d) solidificar la composición obtenida en la etapa c), y producir así una composición particulada sólida.

En otro aspecto, la presente divulgación proporciona el uso de una composición que comprende sulfato de potasio y sulfato de magnesio para producir una composición particulada sólida; en particular, una composición particulada sólida de NPK. Asimismo, se divulga el uso de la composición particulada sólida obtenida mediante un método de acuerdo con cualquiera de las formas de realización divulgadas, como un fertilizante; preferentemente en fertirrigación.

DESCRIPCIÓN DETALLADA DE LA INVENCIÓN

A menos que se defina de otro modo, todos los términos usados en la divulgación de la invención, que incluyen los términos técnicos y científicos, tienen el mismo significado que entiende comúnmente una persona del oficio de nivel medio al que pertenece la presente invención. Para mayor orientación, se incluyen las definiciones de términos para comprender mejor las explicaciones de la presente invención.

Todas las referencias citadas en la presente descripción se incorporan por referencia en su totalidad.

Como se usa en la presente, los términos a continuación tienen los siguientes significados:

Como se usa en la presente, “un”, “una” y “el/la” se refieren a sus referentes singulares y plurales a menos que el contexto indique claramente lo contrario. A modo de ejemplo, “un compartimento” se refiere a un compartimento o a más de un compartimento.

Como se usa en la presente, “alrededor de” en referencia a un valor medible, tal como un parámetro, una cantidad, una duración temporal y similares, incluye variaciones de +/-20% o menos, en particular, +/-10% o menos, más en particular, +/-5% o menos, aún más en particular, +/-1% o menos, e incluso más en particular, +/-0,1% o menos de y desde el valor especificado, siempre que dichas variaciones sean

adecuadas para realizar la invención divulgada. No obstante, cabe destacar que el valor al que el modificador “alrededor de” se refiere también se encuentra específicamente divulgado.

5 Como se usa en la presente, las expresiones “comprenden”, “que comprende”, “comprende” y “comprendido por” son sinónimos de “incluyen”, “que incluye”, “incluye” o “contienen”, “que contiene”, “contiene”, y son expresiones inclusivas o sin limitación que especifican la presencia de lo que sigue, por ejemplo, un componente, y no excluyen o impiden la presencia de componentes, rasgos, elementos, miembros o etapas adicionales no mencionados conocidos en el estado de la técnica o divulgados en la
10 presente.

La mención de rangos numéricos mediante los extremos incluye todos los números y fracciones comprendidos dentro del rango, así como los extremos mencionados.

La expresión “composición particulada sólida” se refiere a una composición que
15 consiste en partículas sólidas. Todas las partículas sólidas de la composición tienen la misma composición química.

En un primer aspecto, la presente divulgación proporciona un método para producir una composición particulada sólida que comprende de 0 a 2,0% en peso de material no hidrosoluble, en donde el método comprende las etapas de: a) mezclar
20 cloruro de potasio (K) y ácido sulfúrico, y producir así una composición que comprende sulfato de potasio y ácido sulfúrico; b) agregar óxido de magnesio a la composición obtenida en la etapa a), y neutralizar así el ácido sulfúrico comprendido en la composición obtenida en la etapa a); c) agregar la composición obtenida en la etapa b) a una composición que comprende nitrógeno (N) y/o fósforo (P); d) solidificar la
25 composición obtenida en la etapa c), y producir así una composición particulada sólida.

El potasio es un elemento importante en la agricultura, y siempre se suministra a los cultivos como una sal de potasio, es decir, K⁺. El cloruro de potasio y el sulfato de potasio son las dos fuentes principales de potasio usadas como fertilizante. El cloruro de potasio puede encontrarse naturalmente y puede producirse a partir de operaciones
30 de minería, pero determinados cultivos no toleran los iones de cloruro, por lo que es preferible usar una fuente de potasio que no sea cloruro de potasio. El sulfato de potasio contiene una fuente de azufre (S), que también es un nutriente que necesita la mayoría de los cultivos, en forma de iones de sulfato. El sulfato de potasio no existe naturalmente y tiene que producirse.

Un método industrial conocido para producir sulfato de potasio se denomina proceso Mannheim. En este proceso, el cloruro de potasio se hace reaccionar con ácido sulfúrico a alta temperatura para obtener sulfato de potasio y cloruro de hidrógeno.

El cloruro de hidrógeno es un gas y se evacúa del recipiente de reacción para después transformarse en una solución acuosa de ácido clorhídrico.

El sulfato de potasio obtenido mediante el proceso aun contiene una pequeña cantidad de ácido sulfúrico, que se usa en exceso en la reacción, y este pequeño exceso debe neutralizarse antes de que el sulfato de potasio pueda usarse para producir un producto fertilizante. Generalmente, la composición que comprende sulfato de potasio y ácido sulfúrico tiene un pH de 1,5 a 2,5, medido como un 10% en peso de solución acuosa. Un pH tan bajo podría no ser conveniente según el uso previsto del sulfato de potasio. Puede preferirse que el sulfato de potasio tenga un pH más cercano a 4.

Habitualmente, esto se realiza agregando una base, en particular, una base inorgánica, tal como óxido de calcio a una solución acuosa que comprende el sulfato de potasio ácido. El óxido de calcio reacciona con el ácido sulfúrico para obtener sulfato de calcio y agua. El óxido de calcio está disponible en el comercio de un amplio rango de proveedores y es relativamente económico. Está disponible como un polvo seco, lo que facilita su uso en una planta industrial. El calcio es un nutriente secundario que muchos cultivos necesitan, por lo que agregar una fuente de calcio en el SOP también brinda un valor agregado agronómico al SOP.

Sin embargo, puede resultar imposible o costoso separar el sulfato de calcio obtenido del sulfato de potasio. Entonces, una composición particulada sólida producida mediante el uso de este sulfato de potasio contiene una cantidad de sulfato de calcio, que tiene una baja hidrosolubilidad (alrededor de 2 a 3 g por litro de agua a 20°C). Esto es inconveniente cuando se trata de producir una composición particulada sólida con una cantidad lo más baja posible de material no hidrosoluble y que comprenda sulfato de potasio.

Se descubrió que el óxido de magnesio es un compuesto muy interesante para reemplazar el óxido de calcio en la etapa de neutralización. El óxido de magnesio es un compuesto alcalino y puede hacerse reaccionar con ácido sulfúrico para neutralizarlo. Cuando el óxido de magnesio reacciona con ácido sulfúrico, se forma sulfato de magnesio, y el sulfato de magnesio tiene una muy buena hidrosolubilidad (al menos 350 g por litro de agua a 20°C). Además, el magnesio es un nutriente necesario para los cultivos, por lo que usar óxido de magnesio en el sulfato de potasio aumenta el valor agronómico del producto fertilizante final.

Asimismo, el óxido de magnesio está disponible fácilmente en grandes cantidades, puede obtenerse como un producto de flujo libre, lo que facilita su adición en el proceso industrial.

5 La cantidad exacta de óxido de magnesio que se agrega al sulfato de potasio puede depender de varios factores, tal como el exceso de ácido sulfúrico usado en la reacción con cloruro de potasio, y el pH deseado del sulfato de potasio después de la etapa de neutralización.

10 La composición que comprende sulfato de potasio y óxido de magnesio se mezcla, para que el óxido de magnesio pueda reaccionar completamente con el ácido sulfúrico.

En una forma de realización, el pH de una solución acuosa al 10% en peso de la composición obtenida después de la neutralización del óxido de magnesio es de 3,5 a 4,5, en particular, de 3,7 a 4,2. Se descubrió que un pH de alrededor de 4 para el sulfato de potasio neutralizado es muy bueno para producir productos fertilizantes, en particular, productos fertilizantes NPK.

15 En una forma de realización, en la etapa b), de 5 a 35 kg, de 5 a 30 kg, de 10 a 35 kg, o de 10 a 30 kg, o de 15 a 25 kg de óxido de magnesio por tonelada de composición obtenida en la etapa a) se agrega a la composición obtenida en la etapa a).

20 Después de la etapa de neutralización, el contenido de agua del sulfato de potasio puede reducirse para permitir que el transporte sea más fácil. Esto puede lograrse mediante diferentes maneras conocidas en el campo técnico, tal como el calentamiento del sulfato de potasio, para que el agua se evapore.

25 El contenido final de agua del sulfato de potasio puede variar según la aplicación deseada del sulfato de potasio.

En una forma de realización, el contenido de agua de la composición obtenida en la etapa b) es de 0,01 a 0,5% en peso, en particular, de 0,05 a 0,5% en peso, más en particular, de 0,05 a 0,25% en peso; incluso más en particular, de 0,05 a 0,23% en peso.

30 La etapa de neutralización puede comprender una etapa de secado, en donde el contenido de agua del sulfato de potasio se reduce al nivel deseado. La etapa de neutralización y la etapa de secado pueden realizarse en un aparato único, tal como un tambor de neutralización.

35 En una forma de realización, el contenido de agua de la composición obtenida en la etapa a) es de 0,001 a 0,5% en peso, en particular, de 0,001 a 0,1% en peso.

Cuando el sulfato de potasio tiene las características deseadas, tal como pH y contenido de agua, puede agregarse a una composición que contiene nitrógeno y/o fósforo. La composición se mezcla hasta que el sulfato de potasio está disperso uniformemente en la composición que comprende N y/o P.

5 En una forma de realización, el sulfato de potasio se agrega a una composición que contiene nitrógeno y fósforo para finalmente obtener un producto fertilizante NPK.

La composición que contiene nitrógeno y/o fósforo puede obtenerse mediante diferentes métodos conocidos en el estado de la técnica. Por ejemplo, en la industria de fertilizantes, un método adecuado comprende la etapa de mezclar roca de fosfato con
10 una solución que comprende uno o más ácidos inorgánicos seleccionados del grupo que consiste en ácido nítrico, ácido sulfúrico y ácido fosfórico. El ácido inorgánico fuerte disuelve la roca de fosfato y transforma los átomos de fósforo presentes en la roca de fosfato en sales de fosfato hidrosolubles. Cuando la solución comprende al menos ácido nítrico, la solución resultante comprende nitrógeno, del ácido nítrico, y fósforo, de la roca
15 de fosfato. La mezcla obtenida puede procesarse además eliminar material insoluble, por ejemplo, mediante filtración.

La solución obtenida a partir de la reacción de la roca de fosfato con uno o más ácidos inorgánicos puede hacerse reaccionar además amoníaco para neutralizar el ácido libre restante. El amoníaco es una base interesante para usar en este proceso
20 porque se transforma, durante la neutralización, en iones de amonio que son una fuente de nitrógeno de fertilizador. Una vez aplicados al suelo, los cultivos pueden absorber directamente los iones de amonio como fuente de nitrógeno y también pueden transformarse en iones de nitrato mediante las bacterias presentes en el suelo. Los iones de nitrato son la fuente de nitrógeno preferida para los cultivos.

25 De manera alternativa, una mezcla que comprende uno o más ácidos seleccionados del grupo que consiste en ácido nítrico, ácido sulfúrico y ácido fosfórico, pueden prepararse y neutralizarse con una base, tal como amoníaco, en particular, amoníaco anhidro. Tal composición puede prepararse con una cantidad muy baja de material no hidrosoluble si todos los materiales de inicio son de alta pureza, por ejemplo,
30 mayor a 95%, 96%, 97%, 98% o 99%. En una forma de realización, la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) se obtiene al mezclar una composición ácida que comprende un componente seleccionado del grupo que consiste en ácido nítrico, ácido sulfúrico, ácido fosfórico y mezclas de estos, con amoníaco.

En una forma de realización, la composición que comprende nitrógeno (N) y/o
35 fósforo (P) usada en la etapa c) se obtiene al mezclar una composición ácida que

consiste en un componente seleccionado del grupo que consiste en ácido nítrico, ácido sulfúrico, ácido fosfórico y mezclas de estos, con amoníaco.

En una forma de realización, la mezcla de ácido consiste en ácido nítrico, la composición neutralizada solo contiene nitrógeno como nutriente, y después de agregar
5 SOP, se obtiene un fertilizante NKS.

En una forma de realización, la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) comprende una sal de amonio y/o una sal de fosfato.

En una forma de realización, la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) comprende 50 a 99% en peso de sales de amonio y/o
10 sales de fosfato. En una forma de realización, la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) comprende 50 a 99% en peso de un componente seleccionado del grupo que consiste en sales de amonio, sales de fosfato y mezclas de estos. En una forma de realización, la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) comprende 50 a 99% en peso, 60 a 99% en peso, 70 a
15 99% en peso, 80 a 99% en peso o 90 a 99% en peso de un componente seleccionado del grupo que consiste en nitrato de amonio, fosfato de amonio, sulfato de amonio y mezclas de estos.

En una forma de realización, la mezcla de ácido comprende ácido fosfórico, la composición neutralizada contiene nitrógeno y fósforo como nutriente, y después de
20 agregar SOP, se obtiene un fertilizante NPKS.

En una forma de realización, la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) es un fundido o una composición fundida.

En una forma de realización, la composición obtenida en la etapa b) se agrega a una composición que comprende nitrógeno (N) y/o fósforo (P) en una relación en peso
25 de 5:1 a 1:5, de 3:1 a 1:5, de 2:1 a 1:5, de 5:1 a 1:3, de 3:1 a 1:3, de 2:1 a 1:3, de 5:1 a 1:2, de 3:1 a 1:2 o de 2:1 a 1:2. La relación en peso de la composición que comprende sulfato de potasio con respecto a la composición que comprende N y/o P se ajusta según el contenido deseado de las partículas sólidas finales.

En una forma de realización, la mezcla ácida comprende ácido sulfúrico, la
30 composición neutralizada comprende nitrógeno y azufre, de manera que después de agregar SOP, se obtiene un fertilizante NKS.

Otros métodos también pueden proporcionar una composición que comprende nitrógeno y/o fósforo. Por ejemplo, es posible disolver en una solución acuosa sales de fosfato de amonio, tales como fosfato diamónico y fosfato monoamónico.

En una forma de realización, se pueden agregar otras fuentes de nutrientes a la composición, ya sea antes del sulfato de potasio, al mismo tiempo que el sulfato de potasio o después de agregar el sulfato de potasio a la composición que comprende nitrógeno y/o fósforo. Por ende, se pueden agregar más nutrientes y micronutrientes durante la etapa c) o a la composición obtenida en la etapa c).

Los cultivos requieren varios tipos de nutrientes: nutrientes primarios, nitrógeno, fósforo y potasio; nutrientes secundarios, calcio, magnesio y azufre; y micronutrientes, boro, manganeso, molibdeno, hierro y zinc. Es habitual que los productos fertilizantes incluyan varios tipos de nutrientes, ya que tales productos fertilizantes reducen el número de aplicaciones que el agricultor debe realizar para suministrar todos los nutrientes necesarios a sus cultivos.

Para cada nutriente, se conocen en el campo técnico una variedad de fuentes adecuadas. Por ejemplo, algunas fuentes adecuadas de magnesio incluyen sulfato de magnesio, kieserita y óxido de magnesio. Las fuentes adecuadas de zinc incluyen sulfato de zinc. Las fuentes adecuadas de hierro incluyen sulfato de hierro y quelatos de hierro, tales como tetraetilendiaminatetraacetato de hierro, también denominado Fe(EDTA). Una fuente adecuada de boro es el borato de sodio o tetraborato de sodio, es decir, bórax. Una fuente adecuada de manganeso es sulfato de manganeso.

La composición resultante comprende sulfato de potasio, nitrógeno y/o fósforo. En la industria de los fertilizantes es habitual proporcionar productos fertilizantes como productos sólidos, en particular, como composición particulada sólida.

Para obtener tales partículas sólidas, la composición que comprende sulfato de potasio, nitrógeno y/o fósforo se puede solidificar. La etapa de solidificación se puede llevar a cabo en un número de aparatos diferentes bien conocidos en el campo técnico, por ejemplo, un granulador de tambor, un esferodizador, una torre de granulación o un granulador de lecho fluidizado. En una forma de realización, la etapa d) se lleva a cabo en una torre de granulación, un granulador de tambor, un esferoidizador o un granulador de lecho fluidizado.

La etapa de solidificación puede comprender etapas adicionales, tales como ajustar el contenido de agua de la composición que comprende sulfato de potasio, nitrógeno y/o fósforo, por ejemplo, al calentar la composición que comprende sulfato de potasio, nitrógeno y/o fósforo.

En una forma de realización, la composición particulada sólida obtenida en la etapa d) es una composición fertilizante particulada sólida, en particular, una composición fertilizante particulada sólida de NK, PK o NPK.

Los fertilizantes NPK se pueden preparar con un amplio rango de relaciones para cada elemento, por ejemplo, 18-4-19, 13-4-25, 15-15-15, 16-10-16, 18-5-18 o 9-5-26, en donde el primer número indica el % en peso de nitrógeno del fertilizante, el segundo número indica el % en peso de fósforo, expresado como P_2O_5 , y el tercer número indica el % en peso de potasio, expresado como K_2O .

En una forma de realización, la composición particulada sólida obtenida en la etapa d) comprende de 0 a 30% en peso, de 5 a 30% en peso, de 10 a 30% en peso, de 0 a 20% en peso, de 5 a 20% en peso, de 10 a 20% en peso, o de 10 a 25% en peso de nitrógeno.

En una forma de realización, la composición particulada sólida obtenida en la etapa d) comprende de 0 a 30% en peso, de 5 a 30% en peso, de 10 a 30% en peso, de 0 a 20% en peso, de 5 a 20% en peso, de 10 a 20% en peso, o de 10 a 25% en peso de fósforo, expresado como P_2O_5 .

En una forma de realización, la composición particulada sólida obtenida en la etapa d) comprende de 0 a 36% en peso, de 5 a 30% en peso, de 10 a 30% en peso, de 0 a 20% en peso, de 5 a 20% en peso, de 10 a 20% en peso, o de 10 a 25% en peso de potasio, expresado como K_2O .

En una forma de realización, la composición particulada sólida obtenida en la etapa d) de 1 a 30% en peso, o de 1 a 20% en peso de cada N, P (expresado como P_2O_5) y K (expresado como K_2O).

La composición particulada sólida resultante obtenida mediante el método descrito anteriormente tiene un contenido menor de material no hidrosoluble que un producto similar obtenido mediante un método que usa sulfato de potasio neutralizado con óxido de calcio, porque no contiene el sulfato de calcio no hidrosoluble.

En una forma de realización, la composición particulada sólida obtenida en la etapa d) comprende de 0 a 2,0% en peso, de 0,001 a 2,0% en peso, de 0,01 a 2,0% en peso, de 0 a 1,5% en peso, de 0,01 a 1,5% en peso, de 0 a 1,0% en peso, de 0 a 0,9% en peso, de 0 a 0,8% en peso, de 0 a 0,7% en peso o de 0 a 0,6% en peso de material no hidrosoluble.

En una forma de realización, la composición particulada sólida obtenida en la etapa d) comprende de 0 a 1,0% en peso, de 0 a 0,9% en peso, de 0 a 0,8% en peso, de 0 a 0,7% en peso, de 0 a 0,6% en peso, de 0 a 0,5% en peso, de 0 a 0,4% en peso, de 0 a 0,3% en peso, de 0 a 0,2% en peso o de 0 a 0,1% en peso de sulfato de calcio.

En una forma de realización, el método comprende además la etapa de aplicar una composición de recubrimiento a la composición particulada sólida obtenida en la

etapa d). Se conoce, en particular, en la industria de los fertilizantes, que agregar una composición de recubrimiento a partículas sólidas mejora las propiedades de las partículas, tal como absorción de humedad reducida, tendencia al apelmazamiento reducida, formación de polvo reducida.

5 Las composiciones de recubrimiento son conocidas en el campo técnico y se seleccionan según la composición de las partículas sólidas y/o del efecto deseado.

En una forma de realización, la composición de recubrimiento comprende un aceite, en particular, un aceite vegetal o un aceite mineral.

10 En una forma de realización, la composición de recubrimiento comprende una cera.

En una forma de realización, la composición de recubrimiento comprende un glicol o un glicol éter.

En otro aspecto, la presente divulgación proporciona el uso de una composición que comprende sulfato de potasio y sulfato de magnesio para producir una composición
15 particulada sólida, en particular, una composición particulada sólida de NPK.

En otro aspecto, la presente divulgación proporciona el uso de la composición particulada sólida obtenida mediante el método descrito anteriormente como un fertilizante, en particular, en fertirrigación. La composición particulada sólida obtenida mediante el método descrito anteriormente es una composición NK, PK o NPK
20 adecuada para ser usada como fertilizante ya que contiene dos o tres de los nutrientes primarios requeridos para cultivos. La composición se puede preparar con una cantidad muy pequeña de material no hidrosoluble, que la hace adecuada para su uso en fertirrigación.

Ejemplo 1: Se preparó un lote de sulfato de potasio en las siguientes
25 condiciones: 1000 kg de cloruro de potasio se mezclaron en un horno con 380 kg de ácido sulfúrico a una temperatura de alrededor de 570°C. Se evacuó el gas de cloruro de hidrógeno del horno y se obtuvo una composición que contenía sulfato de potasio y ácido sulfúrico y se dirigió a un tambor de neutralización. Se agregó 1 - 3% en peso de óxido de magnesio al tambor y el tambor se mezcló durante 20 min. El pH y el contenido
30 de agua del sulfato de potasio se midieron mediante técnicas estándar: pH = 4 (10% en peso de solución acuosa) y contenido de agua = 0,1% en peso. Se preparó una solución al 10% en peso del SOP obtenido y se midió la cantidad de material no hidrosoluble presente en la solución: 0,20% en peso del peso total del SOP presente en la solución.

Se preparó una mezcla de ácido nítrico, ácido sulfúrico y ácido fosfórico con una
35 relación en peso de 5,7/1/1,07 (ácido nítrico/ácido sulfúrico/ácido fosfórico). Se agregó

amoníaco a la mezcla en una relación en 1/3,5 en peso (amoníaco/suma de ácidos) y los componentes se mezclaron hasta obtener una mezcla homogénea de NPS. El sulfato de potasio preparado anteriormente se agregó a la composición de NPS en una relación en peso de 1,2/1 (composición SOP/NPS). Se pueden agregar a la composición

5 nutrientes secundarios y micronutrientes tales como sulfato de magnesio, sulfato de zinc y/o bórax. El fundido resultante se dirigió a un tambor de granulación para producir una composición particulada sólida con un contenido de NPK de 13/4/25.

Se preparó una solución acuosa que contenía 10% en peso de estos gránulos y se midió la cantidad de partículas no hidrosolubles: 0,56% en peso de peso total de los

10 gránulos.

Se produjo con SOP un producto de NPK con el mismo contenido de NPK en donde el óxido de calcio se usó como agente neutralizante, y el producto de NPK final contenía 1,1% en peso de partículas no hidrosolubles.

Ejemplo 2:

15 Siguiendo el procedimiento tanto para el SOP como para los gránulos de NPK, se produjeron productos con las siguientes relaciones de NPK: 18/5/18 y 18-4-19. La cantidad de partículas no hidrosolubles en estos productos fue de 0,60% en peso para 18/5/18 y 0,49% en peso para 18/4/19.

Se produjeron productos con relaciones de NPK idénticas con SOP producido con óxido de calcio, y se descubrió que la cantidad de partículas no hidrosolubles fue

20 de 1,6% en peso para 18/5/18 y 1,0% en peso para 18/4/19.

Ejemplo 3: Se preparó sulfato de potasio como en el ejemplo 1.

Se preparó una mezcla de ácido nítrico, ácido sulfúrico y ácido fosfórico con una relación en peso de 19/1/6,8 (ácido nítrico/ácido sulfúrico/ácido fosfórico). Se agregó

25 amoníaco a la mezcla en una relación en 1/3,6 en peso (amoníaco/suma de ácidos) y los componentes se mezclaron hasta obtener una mezcla homogénea de NPS. El sulfato de potasio preparado anteriormente se agregó a la composición de NPS en una relación en peso de 1/1,6 (composición SOP/NPS). Se pueden agregar a la composición nutrientes secundarios y micronutrientes tales como sulfato de magnesio, sulfato de zinc

30 y/o bórax. El fundido resultante se dirigió a un tambor de granulación para producir una composición sólida y particulada con un contenido de NPK de 16/10/16.

REIVINDICACIONES

1. Un método para producir una composición particulada sólida que comprende de 0 a 2,0% en peso de material no hidrosoluble, en donde el método comprende las etapas de:
 - 5 a) mezclar cloruro de potasio (K) y ácido sulfúrico, y producir así una composición que comprende sulfato de potasio y ácido sulfúrico;
 - b) agregar óxido de magnesio a la composición obtenida en la etapa a), y neutralizar así el ácido sulfúrico comprendido en la composición obtenida en la etapa a);
 - c) agregar la composición obtenida en la etapa b) a una composición que
10 comprende nitrógeno (N) y/o fósforo (P);
 - d) solidificar la composición obtenida en la etapa c), y producir así una composición particulada sólida.
2. El método de acuerdo con la reivindicación 1, en donde el pH de una solución acuosa al 10% en peso de la composición obtenida en la etapa b) es de 3,5 a 4,5, en
15 particular, de 3,7 a 4,2.
3. El método de acuerdo con la reivindicación 1 o 2, en donde, en la etapa b), de 15 a 25 kg de óxido de magnesio por tonelada de composición obtenida en la etapa a) se agregan a la composición obtenida en la etapa a).
4. El método de acuerdo con cualquiera de las reivindicaciones 1 a 3, en donde
20 el contenido de agua de la composición obtenida en la etapa b) es de 0,05 a 0,5% en peso, en particular, de 0,05 a 0,23% en peso.
5. El método de acuerdo con cualquiera de las reivindicaciones 1 a 4, en donde la composición particulada sólida obtenida en la etapa d) es una composición fertilizante particulada sólida, en particular, una composición fertilizante particulada sólida de NK,
25 PK o NPK.
6. El método de acuerdo con cualquiera de las reivindicaciones 1 a 5, en donde la etapa d) se lleva a cabo en una torre de granulación, un granulador de tambor, un esferoidizador o un granulador de lecho fluidizado.
7. El método de acuerdo con cualquiera de las reivindicaciones 1 a 6, en donde
30 la composición que comprende nitrógeno y/o fósforo comprende además un nutriente secundario y/o un micronutriente.
8. El método de acuerdo con cualquiera de las reivindicaciones 1 a 7, que comprende además la etapa de agregar un nutriente secundario y/o un micronutriente durante la etapa c); o a la composición obtenida en la etapa c).

9. El método de acuerdo con cualquiera de las reivindicaciones 1 a 8, en donde la composición que comprende nitrógeno (N) y/o fósforo (P) usada en la etapa c) se obtiene al mezclar una composición ácida que comprende un componente seleccionado del grupo que consiste en ácido nítrico, ácido sulfúrico, ácido fosfórico y mezclas de estos, con amoníaco.

10. El método de acuerdo con cualquiera de las reivindicaciones 1 a 9, que comprende además la etapa de aplicar una composición de recubrimiento a la composición particulada sólida obtenida en la etapa d).

11. El uso de una composición que comprende sulfato de potasio y sulfato de magnesio para producir una composición particulada sólida, en particular, una composición particulada sólida de NPK.

12. El uso de la composición particulada sólida obtenida mediante el método de acuerdo con cualquiera de las reivindicaciones 1 a 9 como un fertilizante, en particular, en fertirrigación.

RESUMEN

La presente divulgación proporciona un método para producir una composición particulada sólida que comprende de 0 a 2,0% en peso de material no hidrosoluble, en donde el método comprende las etapas de: a) mezclar cloruro de potasio y ácido sulfúrico, y producir así una composición que comprende sulfato de potasio y ácido sulfúrico; b) agregar óxido de magnesio a la composición obtenida en la etapa a), y neutralizar así el ácido sulfúrico comprendido en la composición obtenida en la etapa a); c) agregar la composición obtenida en la etapa b) a una composición que comprende nitrógeno (N) y/o fósforo (P); d) solidificar la composición obtenida en la etapa c), y producir así una composición particulada sólida que comprende potasio, nitrógeno y/o fósforo.



(51) International Patent Classification:

C05D 1/02 (2006.01)

C05B 17/00 (2006.01)

C05G 5/23 (2020.01)

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

(21) International Application Number:

PCT/EP2022/078604

Published:

— with international search report (Art. 21(3))

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(22) International Filing Date:

14 October 2022 (14.10.2022)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

21202918.5

15 October 2021 (15.10.2021)

EP

(71) Applicant: YARA INTERNATIONAL ASA [NO/NO];

Drammensveien 131, 0277 Oslo (NO).

(72) Inventors: WIERINGA, Guido; Yara Vlaardingen,

Zevenmanshaven Oost 67, 3133 CA Vlaardingen (NL).

CAMARGO HORTA DE MACEDO, Alexandre; Yara

UK - Pocklington, Manor Place, Wellington Road The In-

dustrial Estate, York YO42 1DN (GB).

(74) Agent: DE CLERCQ & PARTNERS et al.; Edgard

Gevaertdreef 10a, 9830 Sint-Martens-Latem (BE).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE,

KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU,

LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG,

NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,

RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,

TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,

ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, CV,

GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,

TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,

TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,

DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,

LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI,

SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,

GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: METHOD FOR PRODUCING A POTASSIUM-CONTAINING FERTILIZER WITH A LOW CONTENT OF WATER-INSOLUBLE MATERIAL

(57) Abstract: The present disclosure provides a method for producing a solid, particulate composition comprising from 0 to 2.0 weight % of water-insoluble material, the method comprising the steps of: a) mixing potassium chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid; b) adding magnesium oxide to the composition obtained in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a); c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or phosphorus (P); d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition comprising potassium, nitrogen and/or phosphorus.



Method for producing a potassium-containing fertilizer with a low content of water-insoluble material

Description

5 Field of the invention

The present invention is related to the field of fertilizer production, in particular the production of NPK fertilizers with a low content of water-insoluble material.

Background of the invention

10 Nitrogen (N), phosphorus (P) and potassium (K) are the three primary nutrients required by most crops to grow. Soils contain naturally various amounts of these nutrients, but in order to achieve optimal growth and yield, farmers often add sources of these nutrients. In addition, crops may also require secondary nutrients (calcium, magnesium and sulphur) and micronutrients (boron, copper, iron, molybdenum, manganese and zinc)

15 Fertilizer products, in particular solid fertilizer products, such as prills or granules, have been used for centuries. Solid fertilizer may comprise one or more nutrients, and fertilizer products containing more than one nutrient have the advantage that they reduce the number of applications to be done for the farmer by providing several nutrients to the crops in a single application.

A NPK fertilizer refers to a product containing all primary nutrients: N, P and K. It exists in different ways and different raw materials can be used to produce these fertilizers. NPK fertilizers are often
20 named in the form of X/Y/Z, wherein X, respectively Y, and Z, is the weight% of N (expressed as nitrogen), respectively P (expressed as P_2O_5), and K (expressed as K_2O).

An important characteristic of solid fertilizers is the amount of water-insoluble material that they contain. It may be an advantage to produce a NPK product with a very low amount, such as less than 1.0 weight%, of water-insoluble material, as such a product may be used in fertigation, wherein
25 the fertilizer product is first dissolved in water and distributed to the crops via the irrigation system. This fertilization method is gaining popularity and interest as it reduces water consumption and allows a very precise fertilizer application. Fertigation requires a fertilizer product that has a low amount of water-insoluble material, as water-insoluble material can clog irrigation lines.

However, fertilizer products with a low amount of water-insoluble material, in particular NPK
30 fertilizer products, are not easy to obtain, in particular where the production method uses potassium sulphate (SOP) as potassium source.

There is a need to provide a new production method that provides a fertilizer product with a low amount of water-insoluble material.

Summary of the invention

5 It was found out that an important source of water-insoluble material in a product, in particular a fertilizer product, using SOP as potassium source was contained in the SOP, in particular wherein the SOP had been prepared by the Mannheim process. In the Mannheim process for SOP production, sulphuric acid is reacted with potassium chloride to yield potassium sulphate. This reaction uses an excess of sulphuric acid to ensure the full conversion of the potassium chloride. However, if the
10 resulting SOP has a pH too low, in particular below pH =3, the subsequent production steps to obtain a fertilizer product may face issues, such as a very high viscosity and/or higher safety risks.

In order to alleviate one or more of these issues, it is important to raise the pH of the SOP to at least 3.5 (measured as 10 weight% aqueous solution). Neutralizing the excess sulphuric acid, and raising the pH of the SOP is conventionally done by adding calcium oxide. However, when calcium
15 oxide reacts with sulphuric acid, calcium sulphate is formed and calcium sulphate has a very low solubility in water, and this increases the amount of water-insoluble material in the SOP, and therefore in the final product.

It was found that it was possible to replace the calcium oxide used to neutralize sulphuric acid with another compound, namely magnesium oxide. Magnesium oxide is also able to react with
20 sulphuric acid and raises the pH of the SOP. An advantage of using magnesium oxide is that it is converted into magnesium sulphate during the neutralization step. Magnesium sulphate has a very good water solubility and does not increase the content of water-insoluble material of the final product.

In a first aspect, the present disclosure provides a method for producing a solid, particulate
25 composition comprising from 0 to 2.0 weight% of water-insoluble material, the method comprising the steps of: a) mixing potassium chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid; b) adding magnesium oxide to the composition obtained in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a); c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or
30 phosphorus (P); d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition.

In another aspect, the present disclosure provides the use of a composition comprising potassium sulphate and magnesium sulphate to produce a solid, particulate composition; in particular a solid,

particulate NPK composition. Also the use of the solid, particulate composition obtained by a method according to any of the disclosed embodiments, as a fertilizer; preferably in fertigation, is disclosed.

Detailed description of the invention

5 Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

10 All references cited in this description are hereby deemed to be incorporated in their entirety by way of reference.

As used herein, the following terms have the following meanings:

"A", "an", and "the" as used herein refers to both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a compartment" refers to one or more than one compartment.

15 "About" as used herein referring to a measurable value such as a parameter, an amount, a temporal duration, and the like, is meant to encompass variations of +/-20 % or less, in particular +/-10 % or less, more in particular +/-5 % or less, even more in particular +/-1 % or less, and still more in particular +/-0.1 % or less of and from the specified value, in so far such variations are appropriate to perform in the disclosed invention. However, it is to be understood that the value to which the modifier
20 "about" refers is itself also specifically disclosed.

"Comprise", "comprising", and "comprises" and "comprised of" as used herein are synonymous with "include", "including", "includes" or "contain", "containing", "contains" and are inclusive or open-ended terms that specifies the presence of what follows e.g. component and do not exclude or preclude the presence of additional, non-recited components, features, element, members,
25 steps, known in the art or disclosed therein.

The recitation of numerical ranges by endpoints includes all numbers and fractions subsumed within that range, as well as the recited endpoints.

The term "solid, particulate composition" refers to a composition consisting of solid particles. All the solid particles of the composition have the same chemical composition.

30 In a first aspect, the present disclosure provides a method for producing a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material, the method comprising the steps of: a) mixing potassium (K) chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid; b) adding magnesium oxide to the composition

obtained in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a); c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or phosphorus (P); d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition.

Potassium is an important element in agriculture, and it is always supplied to crops as a potassium salt, i.e. K^+ . Potassium chloride and potassium sulphate are the two main sources of potassium used as fertilizer. Potassium chloride may be found naturally and be produced from mining operations, but chloride ions are not tolerated by certain crops, so it may be preferred to use a potassium source other than potassium chloride. Potassium sulphate contains a source of sulphur (S), which is also a nutrient required by most crops, in the form of sulphate ions. Potassium sulphate does not exist naturally and has to be produced.

A known industrial method for producing potassium sulphate is called the Mannheim process. In this process, potassium chloride is reacted with sulphuric acid under high temperature to yield potassium sulphate and hydrogen chloride.

Hydrogen chloride is a gas and is evacuated from the reaction vessel to be later transformed into an aqueous solution, hydrochloric acid.

The potassium sulphate obtained by the process still contains a small amount of sulphuric acid, which is used in excess in the reaction, and this small excess needs to be neutralized before the potassium sulphate can be used for producing a fertilizer product. Generally, the composition comprising potassium sulphate and sulphuric acid has a pH of 1.5 to 2.5, measured as a 10 weight% aqueous solution. Such a low pH may not be desirable depending on the intended use of the potassium sulphate. It may be preferred that the potassium sulphate has a pH closer to 4.

Conventionally, this is done by adding a base, in particular an inorganic base, such as calcium oxide to an aqueous solution comprising the acidic potassium sulphate. Calcium oxide reacts with sulphuric acid to yield calcium sulphate and water. Calcium oxide is commercially available from a wide range of suppliers and relatively cheap. It is available as a dry powder, which makes it easy to use in an industrial plant. Calcium is a secondary nutrient that is required by many crops, so adding a source of calcium in the SOP also brought an added agronomical value to the SOP.

However, it may not be possible or economically interesting to separate the calcium sulphate obtained from the potassium sulphate. So, a solid, particulate composition produced using this potassium sulphate contains an amount of calcium sulphate, which has a low water solubility (about 2 to 3 g per liter of water at 20 °C). This is inconvenient when one is trying to produce a solid, particulate composition with an amount of water-insoluble material as low as possible and comprising potassium sulphate.

It was found out that magnesium oxide is a very interesting compound to replace calcium oxide in the neutralization step. Magnesium oxide is an alkaline compound and can react with sulphuric acid to neutralize it. When magnesium oxide reacts with sulphuric acid, magnesium sulphate is formed, and magnesium sulphate has a very good water solubility (at least 350 g per liter of water at 20 °C).

5 Furthermore, magnesium is a nutrient required by crops, so using magnesium oxide in the potassium sulphate increases the agronomical value of the final fertilizer product.

Magnesium oxide is also easily available in large quantities, it can be obtained as a free-flowing product which facilitates its addition in the industrial process.

10 The exact amount of magnesium oxide added to the potassium sulphate may depend on several factors, such as the excess of sulphuric acid used in the reaction with potassium chloride, and the desired pH of the potassium sulphate after the neutralization step.

The composition comprising potassium sulphate and magnesium oxide is mixed, so that magnesium oxide can fully react with sulphuric acid.

15 In one embodiment, the pH of a 10 wt% aqueous solution of the composition obtained after the magnesium oxide neutralization is from 3.5 to 4.5, in particular from 3.7 to 4.2. A pH around 4 for the neutralized potassium sulphate was found to be very good for producing fertilizer products, in particular NPK fertilizer products.

20 In one embodiment, in step b), from 5 to 35 kg, from 5 to 30 kg, from 10 to 35 kg, or from 10 to 30 kg, or from 15 to 25 kg of magnesium oxide per ton of composition obtained in step a) is added to the composition obtained in step a).

After the neutralization step, the water content of the potassium sulphate may be reduced to allow an easier transport. This can be achieved by a number of ways known in the field, such as heating up the potassium sulphate, so that the water evaporates.

25 The final water content of the potassium sulphate may vary depending on the desired application of the potassium sulphate.

In one embodiment, the water content of the composition obtained in step b) is from 0.01 to 0.5 weight%, in particular from 0.05 to 0.5 weight%, more in particular from 0.05 to 0.25 weight%; even more in particular from 0.05 to 0.23 wt%.

30 The neutralization step may comprise a drying step, wherein the water content of the potassium sulphate is reduced to the desired level. The neutralization step and the drying step may be performed in a single apparatus, such as a neutralization drum.

In one embodiment, the water content of the composition obtained in step a) is from 0.001 to 0.5 weight%, in particular from 0.001 to 0.1 weight%.

When the potassium sulphate has the desired characteristics, such as pH, and water content, it can be added to a composition containing nitrogen and/or phosphorus. The composition is mixed until the potassium sulphate is evenly dispersed in the composition comprising N and/or P.

5 In one embodiment, the potassium sulphate is added to a composition containing nitrogen and phosphorus to eventually yield an NPK fertilizer product.

The composition containing nitrogen and/or phosphorus may be obtained by different methods known in the art. For example, in the fertilizer industry, a suitable method comprises the step of mixing phosphate rock with a solution comprising one or more inorganic acids selected from the group consisting of nitric acid, sulphuric acid and phosphoric acid. The strong inorganic acid dissolves
10 the phosphate rock and transforms the phosphorus atoms present in the phosphate rock as water-soluble phosphate salts. When the solution comprises at least nitric acid, the resulting solution comprises nitrogen, from the nitric acid, and phosphorus, from the phosphate rock. The mixture obtained can be further processed to remove insoluble material, for example by filtration.

The solution obtained from the reaction of phosphate rock with one or more inorganic acid
15 may be further reacted with ammonia to neutralize the remaining free acid. Ammonia is an interesting base to use in this process because it is transformed, during the neutralization, into ammonium ions which are a fertilizer source of nitrogen. Once applied to the soil, ammonium ions can be directly absorbed by crops as nitrogen source and they can also be transformed into nitrate ions by bacteria present in the soil. Nitrate ions are the preferred nitrogen source for crops.

20 Alternatively, a mixture comprising one or more acids selected from the group consisting of nitric acid, sulphuric acid, and phosphoric acid, may be prepared and neutralized with a base, such as ammonia, in particular anhydrous ammonia. Such a composition can be prepared with a very low amount of water-insoluble material if all the starting materials are of high purity, for example higher than 95 %, 96%, 97%, 98%, or 99%. In one embodiment, the composition comprising nitrogen (N)
25 and/or phosphorus (P) used in step c) is obtained by mixing an acidic composition comprising a component selected from the group consisting of nitric acid, sulphuric acid, phosphoric acid, and mixtures thereof, with ammonia.

In one embodiment, the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) is obtained by mixing an acidic composition consisting of a component selected from the group
30 consisting of nitric acid, sulphuric acid, phosphoric acid, and mixtures thereof, with ammonia.

In one embodiment, the acid mixture consists of nitric acid, the neutralized composition only contains nitrogen as nutrient, and after adding SOP, a NKS fertilizer is obtained.

In one embodiment, the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) comprises an ammonium salt and/or a phosphate salt.

In one embodiment, the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) comprises 50 to 99 weight% of ammonium salts and/or phosphate salts. In one embodiment, the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) comprises 50 to 99 weight% of a component selected from the group consisting of ammonium salts, phosphate salts and mixtures thereof. In one embodiment, the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) comprises 50 to 99 weight%, 60 to 99 weight%, 70 to 99 weight%, 80 to 99 weight%, or 90 to 99 weight% of a component selected from the group consisting of ammonium nitrate, ammonium phosphate, ammonium sulphate and mixtures thereof.

In one embodiment, the acid mixture comprises phosphoric acid, the neutralized composition contains nitrogen and phosphorus as nutrient, and after adding SOP, a NPKS fertilizer is obtained.

In one embodiment, the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) is a melt or a molten composition.

In one embodiment, the composition obtained in step b) is added to a composition comprising nitrogen (N) and/or phosphorus (P) in a weight ratio of from 5:1 to 1:5, from 3:1 to 1:5, from 2:1 to 1:5, from 5:1 to 1:3, from 3:1 to 1:3, from 2:1 to 1:3, from 5:1 to 1:2, from 3:1 to 1:2, or from 2:1 to 1:2. The weight ratio of the composition comprising potassium sulphate to the composition comprising N and/or P is adjusted depending on the desired content of the final solid particles.

In one embodiment, the acid mixture comprises sulphuric acid, the neutralized composition comprises nitrogen and sulphur, such that after adding SOP, a NKS fertilizer is obtained.

Others methods may also provide a composition comprising nitrogen and/or phosphorus. For example, it is possible to dissolve in an aqueous solution ammonium phosphate salts, such as diammonium phosphate and monoammonium phosphate.

In one embodiment, further nutrient sources may be added to the composition either before potassium sulphate, at the same time as potassium sulphate or after potassium sulphate has been added to the composition comprising nitrogen and/or phosphorus. Thus, further nutrients and micronutrients may be added during step c) or to the composition obtained in step c).

Crops require several types of nutrients: primary nutrients, nitrogen, phosphorus, and potassium; secondary nutrients, calcium, magnesium and sulphur; and micronutrients, boron, manganese, molybdenum, iron, and zinc. It is common for fertilizer products to comprise several types of nutrients, such fertilizer products reduce the number of applications that the farmer needs to perform to supply all the required nutrients to its crops.

For each nutrient, a number of suitable sources are known in the field. For example, suitable sources of magnesium include magnesium sulphate, kieserite, and magnesium oxide. Suitable sources of zinc include zinc sulphate. Suitable sources of iron include iron sulphate and iron chelates, such as

iron tetraethylenediaminetetraacetate, also named Fe(EDTA). A suitable source of boron is sodium borate or sodium tetraborate, i.e. borax. A suitable source of manganese is manganese sulphate.

The resulting composition comprises potassium sulphate, nitrogen and/or phosphorus. In the fertilizer industry it is common to provide fertilizer products as solid products, in particular as solid, particulate composition.

To obtain such solid, particles, the composition comprising potassium sulphate, nitrogen and/or phosphorus may be solidified. The solidification step may be performed on a number of different apparatus well known in the field, for example a drum granulator, a spherodizer, a prilling tower or a fluidized bed granulator. In one embodiment, step d) is performed in a prilling tower, a drum granulator, a spherodizer, or a fluidized bed granulator.

The solidification step may comprise additional steps, such as adjusting the water content of the composition comprising potassium sulphate, nitrogen, and/or phosphorus, for example by heating up the composition comprising potassium sulphate, nitrogen, and/or phosphorus.

In one embodiment, the solid, particulate composition obtained in step d) is a solid, particulate fertilizer composition, in particular a solid, particulate NK, PK, or NPK fertilizer composition.

NPK fertilizers can be prepared with a wide range of ratios for each element, for example, 18-4-19, 13-4-25, 15-15-15, 16-10-16, 18-5-18, or 9-5-26, wherein the first number indicates the weight% of nitrogen of the fertilizer, the second number indicates the weight% of phosphorus, expressed as P_2O_5 , and the third number indicates the weight% of potassium, expressed as K_2O .

In one embodiment, the solid, particulate composition obtained in step d) comprises from 0 to 30 weight%, from 5 to 30 weight%, from 10 to 30 weight%, from 0 to 20 weight%, from 5 to 20 weight%, from 10 to 20 weight%, or from 10 to 25 weight% of nitrogen.

In one embodiment, the solid, particulate composition obtained in step d) comprises from 0 to 30 weight%, from 5 to 30 weight%, from 10 to 30 weight%, from 0 to 20 weight%, from 5 to 20 weight%, from 10 to 20 weight%, or from 10 to 25 weight%, of phosphorus, expressed as P_2O_5 .

In one embodiment, the solid, particulate composition obtained in step d) comprises from 0 to 36 weight%, from 5 to 30 weight%, from 10 to 30 weight%, from 0 to 20 weight%, from 5 to 20 weight%, from 10 to 20 weight%, or from 10 to 25 weight% of potassium, expressed as K_2O .

In one embodiment, the solid, particulate composition obtained in step d) from 1 to 30 weight%, or from 1 to 20 weight% of each N, P (expressed as P_2O_5) and K (expressed as K_2O).

The resulting solid, particulate composition obtained by the method described above has a lower content of water-insoluble material than a similar product obtained by a method using potassium sulphate neutralized with calcium oxide, because it does not contain the water-insoluble calcium sulphate.

In one embodiment, the solid, particulate composition obtained in step d) comprises from 0 to 2.0 weight%, from 0.001 to 2.0 weight%, from 0.01 to 2.0 weight%, from 0 to 1.5 weight%, from 0.01 to 1.5 weight%, from 0 to 1.0 weight%, from 0 to 0.9 weight%, from 0 to 0.8 weight%, from 0 to 0.7 weight%, or from 0 to 0.6 weight% of water-insoluble material.

5 In one embodiment, the solid, particulate composition obtained in step d) comprises from 0 to 1.0 weight%, from 0 to 0.9 weight%, from 0 to 0.8 weight%, from 0 to 0.7 weight%, from 0 to 0.6 weight%, from 0 to 0.5 weight%, from 0 to 0.4 weight%, from 0 to 0.3 weight%, from 0 to 0.2 weight%, or from 0 to 0.1 weight% of calcium sulphate.

10 In one embodiment, the method further comprises the step of applying a coating composition to the solid, particulate composition obtained in step d). It is known, in particular in the fertilizer industry, to add a coating composition to solid particles to improve the properties of the particles, such as reduced moisture absorption, reduced caking tendency, reduced dust formation.

Coating composition are known in the field and are selected depending on the composition of the solid particles, and/or the required effect.

15 In one embodiment, the coating composition comprises an oil, in particular a vegetable oil, or a mineral oil.

In one embodiment, the coating composition comprises a wax.

In one embodiment, the coating composition comprises a glycol or a glycol ether.

20 In another aspect, the present disclosure provides the use of a composition comprising potassium sulphate and magnesium sulphate to produce a solid, particulate composition, in particular a solid, particulate NPK composition.

In another aspect, the present disclosure provides the use of the solid, particulate composition obtained by the method described above as a fertilizer, in particular in fertigation. The solid, particulate composition obtained by the method described above is a NK, PK, or NPK composition
25 suitable to be used as fertilizer since it contains two or three of the primary nutrients required by crops. The composition can be prepared with a very small amount of water-insoluble material, which makes it suitable to be used in fertigation.

Example 1: A batch of potassium sulphate was prepared in the following conditions: 1000 kg of potassium chloride was mixed in a furnace with 380 kg of sulphuric acid at a temperature of about
30 570 °C. Hydrogen chloride gas was evacuated from the furnace and a composition containing potassium sulphate and sulphuric acid was obtained and directed to a neutralization drum. 1 - 3 weight % of magnesium oxide was added to the drum, and the drum was mixed for 20 min. The pH and water content of the potassium sulphate were measured by standard techniques: pH = 4 (10 weight%

aqueous solution), and water content = 0.1 weight%. A 10 weight% solution of the SOP obtained was prepared, and the amount of water-insoluble material in the solution was measured: 0.20 weight% of the total weight of the SOP present in the solution.

A mixture of nitric acid, sulphuric acid and phosphoric acid was prepared with a weight ratio of 5.7/1/1.07 (nitric acid/sulphuric acid/ phosphoric acid). Ammonia was added to the mixture in 1/3.5 weight ratio (ammonia/sum of acids) and the components were mixed until an homogeneous NPS mixture was obtained. The potassium sulphate prepared above was added to the NPS composition in a 1.2/1 weight ratio (SOP/NPS composition). Secondary and micronutrients such as magnesium sulphate, zinc sulphate and/or borax may be added to the composition. The resulting melt was directed to a granulation drum to produce a solid, particulate composition with an NPK content of 13/4/25.

An aqueous solution containing 10 weight% of these granules was prepared and the amount of water-insoluble particles was measured: 0.56 weight% of the total weight of the granules.

A NPK product with the same NPK content was produced with SOP wherein calcium oxide was used as neutralizing agent, and the final NPK product contained 1.1 weight% of water-insoluble particles.

Example 2:

Following the procedure for both the SOP and the NPK granules, products with the following NPK ratios were produced: 18/5/18, and 18-4-19. The amount of water-insoluble particles in these products was 0.60 weight% for the 18/5/18 and 0.49 weight% for the 18/4/19.

Products with identical NPK ratios were produced with SOP produced with calcium oxide, and the amount of water-insoluble particles was found to be 1.6 weight% for the 18/5/18, and 1.0 weight% for the 18/4/19.

Example 3: Potassium sulphate was prepared as in example 1.

A mixture of nitric acid, sulphuric acid and phosphoric acid was prepared with a weight ratio of 19/1/6.8 (nitric acid/sulphuric acid/ phosphoric acid). Ammonia was added to the mixture in 1/3.6 weight ratio (ammonia/sum of acids) and the components were mixed until an homogeneous NPS mixture was obtained. The potassium sulphate prepared above was added to the NPS composition in a 1/1.6 weight ratio (SOP/NPS composition). Secondary and micronutrients such as magnesium sulphate, zinc sulphate and/or borax may be added to the composition. The resulting melt is directed to a granulation drum to produce a solid, particulate composition with an NPK content of 16/10/16.

Claims

1. A method for producing a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material, the method comprising the steps of:
 - a) mixing potassium (K) chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid;
 - b) adding magnesium oxide to the composition obtained in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a);
 - c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or phosphorus (P);
 - d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition.
2. The method according to claim 1, wherein the pH of a 10 wt% aqueous solution of the composition obtained in step b) is from 3.5 to 4.5, in particular from 3.7 to 4.2.
3. The method according to claim 1 or 2, wherein, in step b), from 15 to 25 kg of magnesium oxide per ton of composition obtained in step a) is added to the composition obtained in step a).
4. The method according to any one of claims 1 to 3, wherein the water content of the composition obtained in step b) is from 0.05 to 0.5 weight%, in particular from 0.05 to 0.23 weight%.
5. The method according to any one of claims 1 to 4, wherein the solid, particulate composition obtained in step d) is a solid, particulate fertilizer composition, in particular a solid, particulate NK, PK, or NPK fertilizer composition.
6. The method according to any one of claims 1 to 5, wherein step d) is performed in a prilling tower, a drum granulator, a spherodizer, or a fluidized bed granulator.

7. The method according to any one of claims 1 to 6, wherein the composition comprising nitrogen and/or phosphorus further comprises a secondary nutrient and/or a micronutrient.
- 5 8. The method according to any one of claims 1 to 7, further comprising the step of adding a secondary nutrient and/or a micronutrient during step c); or to the composition obtained in step c).
- 10 9. The method according to any one of claims 1 to 8, wherein the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) is obtained by mixing an acidic composition comprising a component selected from the group consisting of nitric acid, sulphuric acid, phosphoric acid, and mixtures thereof, with ammonia.
- 15 10. The method according to any one of claims 1 to 9, further comprising the step of applying a coating composition to the solid, particulate composition obtained in step d).
11. The use of a composition comprising potassium sulphate and magnesium sulphate to produce a solid, particulate composition, in particular a solid, particulate NPK composition.
- 20 12. The use of the solid, particulate composition obtained by the method according to any one of claims 1 to 9 as a fertilizer, in particular in fertigation.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/078604

A. CLASSIFICATION OF SUBJECT MATTER INV. C05D1/02 C05G5/23 C05B17/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C05D C05G C05B C05C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 828 883 A (CHARLES HENRY JOURDAN)	1-6, 11,
Y	24 February 1960 (1960-02-24)	12
	claims	7-10
	examples 4, 5, 7	

X	DATABASE WPI	11, 12
	Week 201948	
	Thomson Scientific, London, GB;	
	AN 2019-39387K	
	XP002806124,	
	& CN 109 650 947 A (CAO H)	
	19 April 2019 (2019-04-19)	
Y	abstract	7-10

X	US 7 780 941 B1 (LALANCETTE JEAN-MARC [CA]	11, 12
	ET AL) 24 August 2010 (2010-08-24)	
A	column 5, paragraph 2	1-10
	claims 1, 8, 9, 13, 14, 17, 18	

	-/--	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
30 January 2023	07/02/2023	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Rodriguez Fontao, M	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/078604

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 197546 Thomson Scientific, London, GB; AN 1975-76416W XP002806129, & JP S50 68857 A (HIKARI IND KK) 9 June 1975 (1975-06-09)	11, 12
A	abstract -----	1-10
X	DATABASE WPI Week 199911 Thomson Scientific, London, GB; AN 1999-121795 XP002806130, & CN 1 197 039 A (ZHANG Z) 28 October 1998 (1998-10-28)	11, 12
A	abstract -----	1-10
X	DATABASE WPI Week 201525 Thomson Scientific, London, GB; AN 2015-18845V XP002806131, & CN 104 311 164 A (LOMON LAND AGRIC CO LTD) 28 January 2015 (2015-01-28)	11, 12
A	abstract -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/078604

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 828883	A	24-02-1960	GB 828883 A	24-02-1960
			MY 6100095 A	31-12-1961

CN 109650947	A	19-04-2019	NONE	

US 7780941	B1	24-08-2010	CA 2661479 A1	06-10-2010
			US 7780941 B1	24-08-2010

JP S5068857	A	09-06-1975	JP S571518 B2	11-01-1982
			JP S5068857 A	09-06-1975

CN 1197039	A	28-10-1998	NONE	

CN 104311164	A	28-01-2015	NONE	

European Patent Office
Patentlaan 2
2280 HV Rijswijk
Netherlands

Online filing

Sint-Martens-Latem, July 7, 2023

Our Ref. : YARA-236-PCT
Re. : International Patent Application No. PCT/EP2022/078604 filed on October 14, 2022
"Method for producing a potassium-containing fertilizer with a low content of water-insoluble material"
In name of YARA INTERNATIONAL ASA

Dear Dr. Golze,

Further to the International Search Report (ISR) and Written Opinion (WO) dated February 7, 2023, prepared by the European Patent Office on behalf of the International Searching Authority (ISA) in respect of the above-referenced patent application, a reasoned statement and argumentation in support of the claims of the PCT application as originally filed and in response to the Written Opinion is herewith submitted.

Examination under Chapter II is demanded by way of separate letter.

1. Claim amendments

Enclosed herewith is an amended set of claims. While the claims have been amended to more clearly define the claimed subject matter, care has been taken to ensure that the amendments shall not go beyond the disclosure in the international application as filed and complies with Art 34(2)(b) PCT.

Claim 1 has been amended and finds its basis in page 5 lines 1-4 of the PCT application as originally filed.

Claim 11 has been amended and finds its basis in page 5 lines 12-17 of the PCT application as originally filed.

MAIN OFFICE

Edgard Gevaertdreef 10a
B-9830 Sint-Martens-Latem
Belgium

HASSELT BRANCH

Corda Campus
Kempische Steenweg 309 bus 2.01
B-3500 Hasselt
Belgium

LEUVEN BRANCH

Groenveldstraat 13
B-3001 Leuven (Heverlee)
Belgium

2. Novelty (Art. 33 (2) PCT)

In Item V, the WO indicates that the present application does not meet the criteria of Art. 33(1) PCT, because the subject matter of claims 1-12 is considered not new in the sense of Art. 33(2) PCT.

In particular, with respect to independent claim 1 (and dependent claims 2-10), the Examiner considers that D1 (GB828883A) discloses the use of dolomite and therefore anticipates the feature concerning the addition of magnesium oxide (MgO) in the method to produce a solid, particulate composition of claim 1.

The Applicant respectfully disagrees herewith and submits that present **claim 1** is novel over D1.

In particular, the Applicant notes that the statements made in the WO did not fully consider the multiple differences between the subject-matter of claim 1 and D1. More specific, the Applicant notes that D1 does not disclose the addition of magnesium oxide (MgO), as such, to neutralize the acid sludge (i.e. comprising sulfuric acid). Indeed, D1 does not refer to magnesium oxide but refers to dolomite, which according to page 5 line 86 contains up to 45% MgCO_3 and 55% CaCO_3 . In contrast to what the examiner asserts, example 4 of D1 states on page 5 line 120-121 that the product (and not dolomite) contains 1% of magnesium oxide. Whether dolomite contains magnesium oxide or not is not disclosed in D1. Stated differently, D1 as such does not indicate how magnesium oxide was obtained or produced. Hence, the WO implicitly assumes that magnesium oxide was added, released, or produced in the process disclosed in D1.

Irrespective of this assumption, D1 does not disclose, let alone provide an enabling disclosure, that magnesium oxide reacts with sulfuric acid (emphasis added). In contrast, as mentioned above, example 4 of D1 states that the product contains 1% of magnesium oxide. Present claim 1 further specifies this difference by addition of the following feature: *“such that the magnesium oxide reacts with the sulphuric acid present in the composition produced in step a)”*. Claim 1 thus, at least, differs from D1 in that D1 does not disclose that MgO reacts with sulphuric acid present in the composition.

Moreover, present claim 1 further differs from D1 in that the produced solid, particulate composition comprises from 0 to 2.0 weight% of water-insoluble material. As stated on page 2 line 15-17 of the originally filed PCT application, calcium sulphate (CaSO_4) is a compound that raises the amount of water-insoluble material in a solid particulate composition. Page 5 lines 102-112, Example 4 of D1 refers to the conversion of CaCO_3 , present in dolomite, to CaSO_4 . It is well known within the state of the art that the amount of CaCO_3 in dolomite may vary from 40-60%, which is confirmed in D1 (page 2, lines 85-86) where it is stated that dolomite contains up to 45% MgCO_3 and 55% CaCO_3 . Hence, large amounts of water-insoluble CaSO_4 will intrinsically be present in the produced compositions of D1, which will greatly exceed the upper limit of 2.0 weight% of water-insoluble material as recited in present claim 1.

Hence, in view of the multiple distinguishing features cited above, it is submitted that the subject matter of claim 1 is novel over D1. Similar considerations apply *mutatis mutandis* to dependent claims 2-10 which, according to their direct dependence to novel claim 1, are also novel over D1.

Present independent claim 11 has been amended to include that a 10 wt% aqueous solution of the composition comprising potassium sulphate and magnesium sulphate has a pH from 3.5 to 4.5, in particular from 3.7 to 4.2. D1 does not disclose a selected or preferred sub-range of pH, but refers to an acidic sludge and neutralizing said sludge in general (see e.g. example 4 of D1). Similarly D2 (CN 109650947 A), D3 (US 7780941 B1), D4 (JP S50 68857 A), D5 (CN 1197039 A), and D6 (CN 104311164 A) do not disclose the selected or preferred sub-range of pH, but refer to an acidic composition and neutralizing said composition. The subject matter of claim 11 is thus novel over D1-D6.

It is submitted that present claim 12 is novel over D1-D6, because said claim discloses the use of the solid particulate composition obtained by the method of novel claim 1 as a fertilizer, in particular in fertigation.

3. Inventive step (Art. 33(3) PCT)

In Item V, the WO further indicates that the present application does not involve an inventive step in the sense of Art. 33(3) PCT in view of the cited prior art documents.

As elaborated above, amended claims 1-12 are novel under Art 33(2) PCT over D1 to D6. Moreover, applicant respectfully submits that amended claims 1-12 are inventive under under Art 33(3) PCT over D1 to D6.

Claim 1 of the present PCT application is directed to a method for producing a solid, particulate composition and clearly differs from what is disclosed in D1 in that claim 1 at least refers to *a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material*. Moreover, claim 1 further differs in that it is characterized by the step of *adding magnesium oxide (MgO) to a composition (comprising potassium sulphate and sulphuric acid) such that it reacts with the sulphuric acid present in the composition and neutralizes it*.

The present application teaches that there is a need to produce solid NPK fertilizers with a low amount of water-insoluble material so the product may be used in fertigation, wherein the fertilizer product is first dissolved in water and distributed to the crops via the irrigation system. This fertilization method is gaining popularity and interest as it reduces water consumption and allows a very precise fertilizer application. Fertigation requires a fertilizer product that has a low amount of water-insoluble material, as water-insoluble material can clog irrigation lines (page 1 lines 22-28).

It was found out that an important source of water-insoluble material is generated when neutralizing the excess of sulphuric acid in the production process by adding calcium oxide (CaO) and forming calcium sulphate (CaSO₄) (page 2 lines 13-17).

The inventors have found that the above-listed distinguishing feature of adding magnesium oxide (MgO) such that it reacts with sulphuric acid, thereby neutralizing excess sulphuric acid in the production process, instead of calcium oxide (CaO), results in the formation of highly water soluble magnesium sulphate. Advantageously, the formed magnesium sulphate does not increase the water-insoluble content of the obtained solid-particulate composition (page 2 lines 18-23).

Starting from D1, an objective technical problem can therefore be formulated as how to provide an improved method to produce a NPK fertilizer with a low amount of water-insoluble material. The solution to this problem is given by the method of present claim 1, which implements the step of adding magnesium oxide (MgO) to a composition (comprising potassium sulphate and sulphuric acid) such that it reacts with the sulphuric acid present in the composition and neutralizes it.

The present solution is not found in D1, and is not obvious starting from the disclosures of D1. Instead, D1 teaches in example 4, 5, and 7 the addition of dolomite to the acidic composition (i.e. acid sludge), which according to page 5 line 86 of D1 contains up to 45% MgCO₃ and 55% CaCO₃. Similar to the disadvantageous addition of CaO, CaCO₃ reacts with sulphuric acid to form CaSO₄, hence intrinsically increasing the content of water-insoluble material. D1 therefore actively teaches away from the present solution, which forms MgSO₄ instead of CaSO₄, and does not contain any pointer or motivation to change the process of D1 to arrive at the method of claim 1.

The solution is also not to be found in D2, and is not obvious starting from the disclosures of D2. D2 teaches the use of potassium hydrogen sulfate as fertilizer, and does not suggest to incorporate the mixture obtained in a production process to prepare an NK or PK fertilizer, so a skilled person trying to solve the problem solved by claim 1 would not look at D2 because it is not related to the same field. Even if a skilled person would look at D2 (*quod non*), he would not find any hint to the technical problem to be solved as D2 is not concerned with the content of water-insoluble material in the final product.

The solution is also not to be found in D3, and is not obvious starting from the disclosures of D3. D3 does not refer to the content of water-insoluble material in a NPK fertilizer. In fact, D3 does not disclose a method to produce a NPK fertilizer, but discloses a method to produce a potassium magnesium sulfate fertilizer material. So a skilled person would not look at D3 when trying to solve the technical problem.

The solution is also not to be found in D4, and is not obvious starting from the disclosures of D4. D4 discloses a method wherein dried sewage sludge is mixed with potassium chloride, phosphoric acid and sulfuric acid. D4 does not refer to water-insoluble components and does not disclose the addition of magnesium oxide to a mixture of potassium sulfate and sulfuric acid.

The solution is also not to be found in D5, and is not obvious starting from the disclosures of D5. D5 discloses a method to produce, and separately recover, potassium magnesium sulfate and magnesium chloride. Again, D5 does not suggest to use its final product to prepare an NP or a PK fertilizer. Hence, a skilled person trying to solve the problem solved by claim 1 would not look at D5 because it is not related to the same field.

The solution is also not to be found in D6, and is not obvious starting from the disclosures of D6. D6 does not refer to the content of water-insoluble material in a NPK fertilizer. In fact, D6 does not disclose a method to produce a NPK fertilizer, but discloses a method to produce a potassium magnesium sulfate fertilizer material. So a skilled person would not look at D6 when trying to solve the technical problem.

Summarized, there is *a priori* no reason why the skilled person would consult D1-D6 to arrive at the solution of the present invention. **Claim 1** of the present application is therefore inventive under Art. 33(3) PCT in view of D1-D6.

Similar considerations apply *mutatis mutandis* to the subject matter of **present claims 2-10, and 12**, which is likewise inventive under Art. 33(3) PCT, in view of the cited prior art, because of the direct or indirect dependency of claims 2-10, and 12 to inventive claim 1.

Present independent **claim 11** differs from D1 in that it refers to a *composition comprising potassium sulphate and magnesium sulphate* to produce a solid, particulate composition, in particular a solid, particulate NPK composition; and wherein a 10 wt% aqueous solution of the composition comprising potassium sulphate and magnesium sulphate has a pH from 3.5 to 4.5, in particular from 3.7 to 4.2.

It is highlighted in the present application on page 5 line 15-17 that the technical effect associated with a pH around 4 for (a neutralized) potassium sulphate composition was that it was found to be very good for producing fertilizer products, in particular NPK fertilizer products.

None of the cited documents D1-D6 refer to a pH sub-range, nor specify a preferred sub-range. Hence, none of the documents D1-D6 hint or suggest to use said composition to produce a solid, particulate composition, let alone a NPK composition.

Summarized, there is *a priori* no reason why the skilled person would consult D1-D6 to arrive at the subject matter of present claim 11. Present claim 11 is therefore inventive under Art. 33(3) PCT in view of D1-D6.

4. Requests

The Applicant respectfully submits that the pending claims fulfill the requirements of the PCT and favorable reconsideration of this application is requested.

Should the International Preliminary Examination Authority not agree, or should a negative statement be considered, the above argumentation notwithstanding, an additional opportunity for submitting arguments and/or amendments is requested under Rule 66.4(b) PCT.

In that case, it is preferred that the matter is settled in an interview, either by telephone, or by videoconference.

The observations contained in the present letter, are made solely for the purposes of the prosecution of this International patent application and without prejudice of the Applicant to National or regional jurisdictions.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'K. Pappaert', with a stylized flourish above it.

Mr. Kris Pappaert
Ms. Lieve Coenegrachts
Professional representatives before the European Patent Office

Encl.: Amended claims, version showing amendments and retyped version

European Patent Office
Patentlaan 2
2280 HV Rijswijk
Netherlands

Online filing

Sint-Martens-Latem, November 7, 2023

Our Ref. : YARA-236-PCT
Re. : International Patent application No PCT/EP2022/078604 filed on 14 October 2022
"Method for producing a potassium-containing fertilizer with a low content of water-insoluble material"
In name of YARA INTERNATIONAL ASA

Dear Dr. Rodriguez,

Further to the Written Opinion (WO) of the International Preliminary Examination Authority (IPEA) dated September 14, 2023, in respect of the above-referenced patent application, a reasoned statement in support of the claims on file is herewith submitted, in accordance to Rule 66.3 (a) PCT.

1. Novelty (Art. 33(2) PCT)

The Applicant gratefully accepts the acknowledgement of novel subject matter for claims 1-12 currently on file. Therefore, the present claims comply with **Art. 33(2) PCT**.

2. Inventive step (Art. 33(3) PCT)

In Item V, the WO indicates that the present application does not satisfy the requirements of Art. 33(3) PCT because the subject matter of claim 1 does not involve an inventive step in view of D1 (GB828883A) or in view of D1 in combination with D3 (US7780941 B1), D4 (JPS5068857 A), D5 (CN1197039 A), or D6 (CN104311164 A). The Applicant respectfully disagrees herewith for at least the reasons described herein below.

Starting from D1, an objective technical problem was formulated by the WO to be:

MAIN OFFICE

Edgard Gevaertdreef 10a
B-9830 Sint-Martens-Latem
Belgium

HASSELT BRANCH

Corda Campus
Kempische Steenweg 309 bus 2.01
B-3500 Hasselt
Belgium

LEUVEN BRANCH

Groenveldstraat 13
B-3001 Leuven (Heverlee)
Belgium

“How to provide a potassium sulphate containing fertilizer with improved solubility, obtained by the reaction and further neutralization of sulphuric acid with potassium chloride?”

The solution to this problem is given by the method for producing a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material as recited in present claim 1.

The present solution is not obvious starting from **D1**. In particular, the Applicant submits that the statements made in the WO of the IPEA did not fully consider the *multiple differences* between the subject matter of claim 1 and what is disclosed in D1.

In general, D1 relates to a process for manufacturing a fertilizer product in which a solid fertilizer raw material (i.e., phosphate rock and/or dolomite) is reacted with a dry acid sludge comprising an inorganic acid material (i.e., sulphuric acid, phosphoric acid and/or gypsum) and a fertilizer ingredient (i.e., NH_3 and/or KCl) (D1: see claims 1-3 and examples 1-9). The purpose of D1 is to carry out said process without extraneously applied heat and artificial drying of the fertilizer product (D1: see p.3 l.33-35).

Page 5, column 1 l. 2-45 of D1 refers to the use of dolomite (*emphasis added*) to furnish water-soluble magnesium, preferably in combination with phosphates. D1 discloses that dolomite may contain up to 55% CaCO_3 (D1: see p.5 l. 86). Hence, a skilled person applying the method of D1 would not arrive at a process for producing a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material with the specific combination of process features as described in present claim 1.

It is noted that the reference made in point 2.6 of Item V of the WO is unclear since in D1 paragraphs [0009]- [0011] are not disclosing a method that is referred to by the examiner. Nevertheless, the Applicant submits that D1 is completely silent about the use of any other solid fertilizer materials or fertilizer ingredients. Hence, there is no pointer or guidance for the skilled person to arrive at the present invention. Based on the teachings of D1, the skilled person would not be motivated to make non-obvious modifications to the process of D1 to arrive at the process recited in present claim 1. Such modifications would only be made using impermissible hindsight.

In view of the above, the skilled person would not have been motivated to change the process of D1 to arrive at the present solution.

The present solution is also not to be found in **D3**. D3 relates to a different process to prepare a different fertilizer composition than what is disclosed in D1 (i.e., potassium magnesium sulfate or SOPM having a different chemical formula than potassium sulfate, D3: see col.1 l.18-47). In particular, D3 explicitly states that the Mannheim process (as disclosed in D1 and the present invention) is undesirable because it is characterized by a too high reaction temperature leading to severe corrosion problems, difficult heat transfer and large energy consumption (D3: see col.1 l.34-47). Hence, the teachings of D1 and D3 stand in heavy discrepancy to each other and they even refer to processing conditions (i.e., temperature ranges, see for instance claim 1 of D3) and a combination of D1 and D3 would thus not be obvious but rather artificial.

Even if the skilled person would consider combining the teachings of D1 and D3, he would still not arrive at the present invention, since D3 does not refer to the formation of a potassium sulphate containing fertilizer, but relates to a process for producing potassium magnesium sulphate comprising reacting sulfuric acid with potassium chloride and magnesium chloride at 100-160 °C (D3: see col.1 l.51-56 and claims 1-9). Moreover, D3 does not refer to the provision of a process for producing a fertilizer composition with a low amount of water-insoluble material. Hence, a skilled person starting from the process of D1 and applying the teaching of D3 would still not arrive at the process for producing a solid, particulate composition having the combination of features as recited in present claim 1.

The present solution is also not to be found in **D4**. D4 relates to a method for producing fertilizer from wire mesh sludge which is produced when organic waste liquid is treated by an activated sludge method. Hence, D4 belongs to a different technical field and the skilled person, aiming to solve the technical problem defined above, would not consult D4.

Even if the skilled person would consider consulting D4 (*quod non*), D4 does not refer to the provision of a fertilizer composition with a low amount of water-insoluble material as recited in present claim 1. A skilled person would not consider combining D1 and D4 in expectation of solving the technical problem. On the contrary, D4 is silent about the use of MgO to neutralize the sulfuric acid in the acidic potassium sulphate composition as recited in present claim 1. Hence, even when combining the teachings of D1 and D4, the skilled person would still not arrive at the present invention.

The present solution is also not to be found in **D5**. D5 relates to a method to produce, and separately recover, potassium magnesium sulfate (SOPM) and magnesium chloride (D5: see example 1-3). Hence, D5 relates to a different process and different fertilizer composition than what is disclosed in D1. In view thereof, a skilled person aiming to provide a potassium sulphate containing fertilizer with improved solubility, would *prima facie* not consider consulting D5.

Even when consulting D5, D5 is silent about the use of MgO to neutralize the sulfuric acid in the acidic potassium sulphate composition as recited in present claim 1. Hence, even when combining the teachings of D1 and D5, the skilled person would still not arrive at the present invention.

The present solution is also not to be found in **D6**. D6 relates to a method to produce a potash magnesium sulfate fertilizer (D6: see §[0002]). Hence, D6 relates to a different process and different fertilizer composition than what is disclosed in D1. In view thereof, a skilled person aiming to provide a potassium sulphate containing fertilizer with improved solubility, would *prima facie* not consider consulting D6.

Even when consulting D6, D6 is silent about the use of MgO to neutralize the sulfuric acid in the acidic potassium sulphate composition as recited in present claim 1. Hence, even when combining the teachings of D1 and D6, the skilled person would still not arrive at the present invention.

In summary, present claim 1 is inventive over D1 alone or in combination with D3, D4, D5, or D6. Similar considerations apply *mutatis mutandis* to claims 2-12 due to their direct or indirect

dependency on novel and inventive claim 1. Therefore, it is submitted that the present claims comply with **Art. 33(3) PCT**.

3. Clarity

Claim 1 is objected because the matter for which protection is sought is allegedly not clearly defined because the passage *"comprising from 0 to 2.0 weight% of water-insoluble material"* is considered as a result-to-be-achieved.

Applicant however disagrees and hereby refers to the description on page 6, l. 20-27, which states *"such a composition can be prepared with a very low amount of water-insoluble material if all the starting materials are of high purity, for example higher than 95%, 96%, 97%; 98% or 99%"*. Therefore, Applicant submits that the technical features necessary to have a composition with maximum 2.0 weight% of water-insoluble material are clear to a skilled person.

4. Requests

The Applicant respectfully submits that the pending claims fulfill the requirements of the PCT and favorable reconsideration of this application is requested.

Should the International Preliminary Examination Authority not agree, or should a negative statement be considered, the above argumentation notwithstanding, an additional opportunity for submitting arguments and/or amendments is requested under Rule 66.4(b) PCT.

In that case, it is preferred that the matter is settled in an interview, either by telephone, or by videoconference.

The observations contained in the present letter, are made solely for the purposes of the prosecution of this International patent application and without prejudice of the Applicant to National or regional jurisdictions.

Respectfully submitted,



Mr. Kris Pappaert
Ms. Lieve Coenegrachts
Professional representatives before the European Patent Office

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION,
OBTENTION OR TRANSMITTAL
OF PRIORITY DOCUMENT
(PCT Administrative Instructions, Section 411)

To:

DE CLERCQ & PARTNERS
Edgard Gevaertdreef 10a
9830 Sint-Martens-Latem
BELGIQUE

Date of mailing (<i>day/month/year</i>) 28 November 2022 (28.11.2022)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference YARA-236-PCT	
International application No. PCT/EP2022/078604	
International publication date (<i>day/month/year</i>) Not yet published	
Applicant YARA INTERNATIONAL ASA	International filing date (<i>day/month/year</i>) 14 October 2022 (14.10.2022) Priority date (<i>day/month/year</i>) 15 October 2021 (15.10.2021)

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
15 October 2021 (15.10.2021)	21202918.5	EP	25 November 2022 (25.11.2022)

The letters "NR" denote a priority document which, on the date of mailing of this Form, had not yet been received or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis). Where the applicant has failed to either submit, request to prepare and transmit, or to request the International Bureau to obtain the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

An asterisk "*" next to a date of receipt, denotes a priority document submitted or transmitted to or obtained by the International Bureau but not in compliance with Rule 17.1(a), (b) or (b-bis) (the priority document was received after the time limit prescribed in Rule 17.1(a); the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b) or the request to the International Bureau to obtain the priority document was made after the applicable time limit under Rule 17.1(b-bis)). Even though the priority document was not furnished in compliance with Rule 17.1(a), (b) or (b-bis), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Nora Lindner e-mail pct.team5@wipo.int Telephone No. +41 22 338 74 05
---	--

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

PCT

To:

De Clercq & Partners
Edgard Gevaertdreef 10a
9830 Sint-Martens-Latem
BELGIQUE

NOTIFICATION OF THE INTERNATIONAL APPLICATION NUMBER AND OF THE INTERNATIONAL FILING DATE

(PCT Rule 20.2(c))

Date of mailing
(day/month/year)

28-11-2022

Applicant's or agent's file reference
YARA-236-PCT

IMPORTANT NOTIFICATION

International application No.

PCT/EP2022/078604

International filing date (day/month/year)

14 October 2022 (14-10-2022)

Priority date (day/month/year)

15 October 2021 (15-10-2021)

Applicant

YARA INTERNATIONAL ASA

Title of the invention

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2. The applicant is further notified that the record copy of the international application:



was transmitted to the International Bureau on see above date of mailing



has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*:



because the necessary national security clearance has not yet been obtained



because (reason to be specified)

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

Name and mailing address of Receiving Office



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040
Fax: (+31-70) 340-3016

Authorized officer

Kutschis, Vanessa

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
De Clercq & Partners Edgard Gevaertdreef 10a 9830 Sint-Martens-Latem BELGIQUE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (PCT Rule 71.1)

Date of mailing
(day/month/year)

01.02.2024

Applicant's or agent's file reference YARA-236-PCT		IMPORTANT NOTIFICATION	
International application No. PCT/EP2022/078604	International filing date (day/month/year) 14.10.2022	Priority date (day/month/year) 15.10.2021	
Applicant Yara International ASA			

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:  European Patent Office Gitschiner Str. 103 D-10958 Berlin Tel. +49 30 25901 - 0 Fax: +49 30 25901 - 840	Authorized Officer Willis, Peggy Tel. +49 30 25901-749	
---	--	---

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference YARA-236-PCT	FOR FURTHER ACTION		See Form PCT/IPEA/416
International application No. PCT/EP2022/078604	International filing date (day/month/year) 14.10.2022	Priority date (day/month/year) 15.10.2021	
International Patent Classification (IPC) or national classification and IPC INV. C05D1/02			
Applicant Yara International ASA			
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>7</u> sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. ☒ a total of <u>8</u> sheets, as follows: ☒ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions). ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2). ☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)). b. ☐ a separate electronic file containing a sequence listing (<i>sent to the International Bureau only</i>)			
4. This report contains indications relating to the following items: ☒ Box No. I Basis of the report ☐ Box No. II Priority ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability ☐ Box No. IV Lack of unity of invention ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement ☐ Box No. VI Certain documents cited ☒ Box No. VII Certain defects in the international application ☒ Box No. VIII Certain observations on the international application			
Date of submission of the demand 07.07.2023		Date of completion of this report 01.02.2024	
Name and mailing address of the international preliminary examining authority:  European Patent Office Gitschiner Str. 103 D-10958 Berlin Tel. +49 30 25901 - 0 Fax: +49 30 25901 - 840		Authorized officer Rodriguez Fontao, M Telephone No. +31 70 340-3758 	

Box No. I Basis of the report

1. With regard to the **language**, this report is based on
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3(a) and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4(a))
 - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))
2. With regard to the **elements*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

Description, Pages

1-10 as originally filed

Claims, Numbers

1-12 filed in electronic form on

07-07-2023

- ☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
5. ☐ This report has been established:
- ☐ taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-bis) and 70.2(e)).
 - ☐ without taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91(Rules 66.4bis and 70.2(e)).

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2022/078604

6. ☒ With regard to top-up searches (Rules 66.1 *ter* and 70.2(f)):
- ☒ A top-up search was carried out by this Authority on 18.01.2024 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
 - ☐ Additional relevant documents have been discovered during the top-up search.
 - ☐ No top-up search was carried out by this Authority because it would serve no useful purpose.
7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

* If item 4 applies, some or all of those sheets may be marked "superseded".

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	<u>7-10, 12</u>
	No: Claims	<u>1-6, 11</u>
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-12</u>
Industrial applicability (IA)	Yes: Claims	<u>1-12</u>
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

D1 GB 828 883 A (CHARLES HENRY JOURDAN) 24 February 1960 (1960-02-24)

D2 DATABASE WPI Week 201948 Thomson Scientific, London, GB; AN 2019-39387K XP002806124, & CN 109 650 947 A (CAO H) 19 April 2019 (2019-04-19)

D3 US 7 780 941 B1 (LALANCETTE JEAN-MARC [CA] ET AL) 24 August 2010 (2010-08-24)

D4 DATABASE WPI Week 197546 Thomson Scientific, London, GB; AN 1975-76416W & JP S50 68857 A (HIKARI IND KK) 9 June 1975 (1975-06-09)

D5 DATABASE WPI Week 199911 Thomson Scientific, London, GB; AN 1999-121795 & CN 1 197 039 A (ZHANG Z) 28 October 1998 (1998-10-28)

D6 DATABASE WPI Week 201525 Thomson Scientific, London, B; AN 2015-18845V & CN 104 311 164 A (LOMON LAND AGRIC CO LTD) 28 January 2015 (2015-01-28)

2 INDEPENDENT CLAIM 1

The present application does not satisfy the requirements set forth in Article 33(3) PCT because the subject matter of claim 1 does not involve an inventive step in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

2.1 D1 is considered to be the closest prior art. This document describes a method comprising the steps of:

- a) mixing potassium (K) chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid;
- b) adding dolomite to the composition obtained in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a);

- c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or phosphorus (P);
d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition (see claims 1,2,4,6; examples 4,5,7).
- 2.2 The difference between the subject-matter of claim 1 and the teaching of D1 lies in the fact that magnesium oxide is added to the composition obtained in step a) whereas in D1 dolomite is used.
- 2.3 The technical effect mentioned by the applicant in the description in relation to the use of magnesium oxide instead of calcium oxide lies in the fact that magnesium sulphate is formed which has a better solubility than calcium sulphate.
- 2.4 In this context, the problem to be solved in view of D1 can be considered as the provision of a potassium sulphate containing fertiliser obtained by the reaction and further neutralization of sulphuric acid with potassium chloride with improved solubility.
- 2.5 Departing from D1 the skilled person would be aware that the neutralization with calcium containing materials such as dolomite would lead to the formation of calcium sulphate in addition to magnesium sulphate. The problem of the solubility of a fertiliser composition is well known to the skilled person that would be prompted to look for soluble fertiliser alternatives if the final product is going to be used, for example, in fertigation instead of cheaper ones if it does not constitute a limiting parameter.
- 2.6 Any skilled person with average chemical skills will have the ability to substitute a generally available agricultural magnesium material, such as dolomite, with an alternative magnesium compound capable of conferring adequate solubility properties to the final product and arrive at the use of magnesium oxide from their own technical knowledge without the exercise of an inventive skill.
- 2.7 Furthermore, this can be seen in numerous documents of the prior art, where the neutralization with magnesium oxide of an acidic reaction product of sulphuric acid with potassium chloride, had already been used. This is the case, for example, of documents D2 (wrongly mentioned as D1 in previous communication; in paragraphs [0009]-[0011]), D5 (abstract) where potassium chloride is stirred in warm water, sulphuric acid is added and the mixture is neutralised with magnesium oxide and D6 (see abstract) where potassium magnesium fertilizer is prepared by reacting potassium chloride and

concentrated sulphuric acid to obtain potassium hydrogen sulfate slurry. The obtained material is neutralised with magnesium oxide material. The obtained material is cooled, crushed, and then dried to obtain the finished product.

- 2.8 There is no information in these documents that would lead to the conclusion that the magnesium oxide had not reacted with the sulphuric acid present, or that the material would not be completely soluble.
- 2.9 It would, therefore, be obvious to the person skilled in the art, namely when the same result is to be achieved, to apply these features with corresponding effect to the method according to D1, thereby arriving to the method according to claim 1.
- 2.10 It is therefore considered that the subject-matter of claim 1 lacks an inventive step in the sense of Article 33(3) PCT.

3 DEPENDENT CLAIMS 2-10

Dependent claims 2-10 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect inventive step (Article 33(3) PCT). The subject-matter of these claims is either known from the combination of documents or considered to be common practice for a man skilled in the art.

- 3.1 The subject-matter of claims 2-6 is known from document D1 (see claims; examples 4,5,7) and lacks therefore an inventive step following the same reasoning used above for the subject-matter of claim 1.
- 3.2 The subject-matter of claims 7-10 is considered to be mere embodiments within the ambit of claim 1 from which they depend. The technical features of said claims have not been shown to substantiate to a technical effect in a non-obvious manner nor a problem has been shown to have been solved by the application of these features. The technical features of this claims are considered as normal practice in the fertiliser field.

4 INDEPENDENT CLAIM 11

Notwithstanding, the observations made below under Item VIII, the present application does not satisfy the requirements set forth in Article 33(3) PCT because the subject matter of claim 1 does not involve an inventive step in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

- 4.1 The same reasoning used above for the subject-matter of claims 1 and 2 applies here, mutatis mutandis.

5 INDEPENDENT CLAIM 12

The present application does not satisfy the requirements set forth in Article 33(3) PCT because the subject matter of claim 12 does not involve an inventive step in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT), departing from D1 and following the same reasoning used above for the subject-matter of claim 1.

Re Item VII

Certain defects in the international application

- 6 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in D1-D6 is not mentioned in the description, nor are these documents identified therein.

Re Item VIII

Certain observations on the international application

- 7 The application does not meet the requirements of Article 6 PCT, because claims 1 and 11 are not clear.
- 7.1 There is a discrepancy between the technical features mentioned in the drafting of independent claims 1 and 11 in the following sense:
- The compositions corresponding, respectively, to the method described in claim 1, and to the use described in claim 11, do not have the same scope, since there is no limitation imposed on the water solubility of the composition in claim 11 nor to the pH of the aqueous solution of the composition in claim 1.
- The present drafting of claims 1 and 11 tends therefore to cast uncertainty as to which are the technical features essential for carrying out the invention and which are the technical features which can be considered as further features relating to different embodiments of the present application.
- 7.2 Furthermore, since solid, particulate compositions comprising potassium sulphate and magnesium sulphate are known in the art, these claims at least formally do not meet the requirements of unity of invention.

European Patent Office
Patentlaan 2
2280 HV Rijswijk
Netherlands

Online filing

Sint-Martens-Latem, July 7, 2023

Our Ref. : YARA-236-PCT
Re. : International Patent Application No. PCT/EP2022/078604 filed on October 14, 2022
"Method for producing a potassium-containing fertilizer with a low content of water-insoluble material"
In name of YARA INTERNATIONAL ASA

Dear Dr. Golze,

Further to the International Search Report (ISR) and Written Opinion (WO) dated February 7, 2023, prepared by the European Patent Office on behalf of the International Searching Authority (ISA) in respect of the above-referenced patent application, a reasoned statement and argumentation in support of the claims of the PCT application as originally filed and in response to the Written Opinion is herewith submitted.

Examination under Chapter II is demanded by way of separate letter.

1. Claim amendments

Enclosed herewith is an amended set of claims. While the claims have been amended to more clearly define the claimed subject matter, care has been taken to ensure that the amendments shall not go beyond the disclosure in the international application as filed and complies with Art 34(2)(b) PCT.

Claim 1 has been amended and finds its basis in page 5 lines 1-4 of the PCT application as originally filed.

Claim 11 has been amended and finds its basis in page 5 lines 12-17 of the PCT application as originally filed.

MAIN OFFICE

Edgard Gevaertdreef 10a
B-9830 Sint-Martens-Latem
Belgium

HASSELT BRANCH

Corda Campus
Kempische Steenweg 309 bus 2.01
B-3500 Hasselt
Belgium

LEUVEN BRANCH

Groenveldstraat 13
B-3001 Leuven (Heverlee)
Belgium

2. Novelty (Art. 33 (2) PCT)

In Item V, the WO indicates that the present application does not meet the criteria of Art. 33(1) PCT, because the subject matter of claims 1-12 is considered not new in the sense of Art. 33(2) PCT.

In particular, with respect to independent claim 1 (and dependent claims 2-10), the Examiner considers that D1 (GB828883A) discloses the use of dolomite and therefore anticipates the feature concerning the addition of magnesium oxide (MgO) in the method to produce a solid, particulate composition of claim 1.

The Applicant respectfully disagrees herewith and submits that present **claim 1** is novel over D1.

In particular, the Applicant notes that the statements made in the WO did not fully consider the multiple differences between the subject-matter of claim 1 and D1. More specific, the Applicant notes that D1 does not disclose the addition of magnesium oxide (MgO), as such, to neutralize the acid sludge (*i.e.* comprising sulfuric acid). Indeed, D1 does not refer to magnesium oxide but refers to dolomite, which according to page 5 line 86 contains up to 45% MgCO_3 and 55% CaCO_3 . In contrast to what the examiner asserts, example 4 of D1 states on page 5 line 120-121 that the product (and not dolomite) contains 1% of magnesium oxide. Whether dolomite contains magnesium oxide or not is not disclosed in D1. Stated differently, D1 as such does not indicate how magnesium oxide was obtained or produced. Hence, the WO implicitly assumes that magnesium oxide was added, released, or produced in the process disclosed in D1.

Irrespective of this assumption, D1 does not disclose, let alone provide an enabling disclosure, that magnesium oxide reacts with sulfuric acid (*emphasis added*). In contrast, as mentioned above, example 4 of D1 states that the product contains 1% of magnesium oxide. Present claim 1 further specifies this difference by addition of the following feature: *“such that the magnesium oxide reacts with the sulphuric acid present in the composition produced in step a)”*. Claim 1 thus, at least, differs from D1 in that D1 does not disclose that MgO reacts with sulphuric acid present in the composition.

Moreover, present claim 1 further differs from D1 in that the produced solid, particulate composition comprises from 0 to 2.0 weight% of water-insoluble material. As stated on page 2 line 15-17 of the originally filed PCT application, calcium sulphate (CaSO_4) is a compound that raises the amount of water-insoluble material in a solid particulate composition. Page 5 lines 102-112, Example 4 of D1 refers to the conversion of CaCO_3 , present in dolomite, to CaSO_4 . It is well known within the state of the art that the amount of CaCO_3 in dolomite may vary from 40-60%, which is confirmed in D1 (page 2, lines 85-86) where it is stated that dolomite contains up to 45% MgCO_3 and 55% CaCO_3 . Hence, large amounts of water-insoluble CaSO_4 will intrinsically be present in the produced compositions of D1, which will greatly exceed the upper limit of 2.0 weight% of water-insoluble material as recited in present claim 1.

Hence, in view of the multiple distinguishing features cited above, it is submitted that the subject matter of claim 1 is novel over D1. Similar considerations apply *mutatis mutandis* to dependent claims 2-10 which, according to their direct dependence to novel claim 1, are also novel over D1.

Present independent claim 11 has been amended to include that a 10 wt% aqueous solution of the composition comprising potassium sulphate and magnesium sulphate has a pH from 3.5 to 4.5, in particular from 3.7 to 4.2. D1 does not disclose a selected or preferred sub-range of pH, but refers to an acidic sludge and neutralizing said sludge in general (see e.g. example 4 of D1). Similarly D2 (CN 109650947 A), D3 (US 7780941 B1), D4 (JP S50 68857 A), D5 (CN 1197039 A), and D6 (CN 104311164 A) do not disclose the selected or preferred sub-range of pH, but refer to an acidic composition and neutralizing said composition. The subject matter of claim 11 is thus novel over D1-D6.

It is submitted that present claim 12 is novel over D1-D6, because said claim discloses the use of the solid particulate composition obtained by the method of novel claim 1 as a fertilizer, in particular in fertigation.

3. Inventive step (Art. 33(3) PCT)

In Item V, the WO further indicates that the present application does not involve an inventive step in the sense of Art. 33(3) PCT in view of the cited prior art documents.

As elaborated above, amended claims 1-12 are novel under Art 33(2) PCT over D1 to D6. Moreover, applicant respectfully submits that amended claims 1-12 are inventive under under Art 33(3) PCT over D1 to D6.

Claim 1 of the present PCT application is directed to a method for producing a solid, particulate composition and clearly differs from what is disclosed in D1 in that claim 1 at least refers to *a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material*. Moreover, claim 1 further differs in that it is characterized by the step of *adding magnesium oxide (MgO) to a composition (comprising potassium sulphate and sulphuric acid) such that it reacts with the sulphuric acid present in the composition and neutralizes it*.

The present application teaches that there is a need to produce solid NPK fertilizers with a low amount of water-insoluble material so the product may be used in fertigation, wherein the fertilizer product is first dissolved in water and distributed to the crops via the irrigation system. This fertilization method is gaining popularity and interest as it reduces water consumption and allows a very precise fertilizer application. Fertigation requires a fertilizer product that has a low amount of water-insoluble material, as water-insoluble material can clog irrigation lines (page 1 lines 22-28).

It was found out that an important source of water-insoluble material is generated when neutralizing the excess of sulphuric acid in the production process by adding calcium oxide (CaO) and forming calcium sulphate (CaSO₄) (page 2 lines 13-17).

The inventors have found that the above-listed distinguishing feature of adding magnesium oxide (MgO) such that it reacts with sulphuric acid, thereby neutralizing excess sulphuric acid in the production process, instead of calcium oxide (CaO), results in the formation of highly water soluble magnesium sulphate. Advantageously, the formed magnesium sulphate does not increase the water-insoluble content of the obtained solid-particulate composition (page 2 lines 18-23).

Starting from D1, an objective technical problem can therefore be formulated as how to provide an improved method to produce a NPK fertilizer with a low amount of water-insoluble material. The solution to this problem is given by the method of present claim 1, which implements the step of adding magnesium oxide (MgO) to a composition (comprising potassium sulphate and sulphuric acid) such that it reacts with the sulphuric acid present in the composition and neutralizes it.

The present solution is not found in D1, and is not obvious starting from the disclosures of D1. Instead, D1 teaches in example 4, 5, and 7 the addition of dolomite to the acidic composition (i.e. acid sludge), which according to page 5 line 86 of D1 contains up to 45% MgCO₃ and 55% CaCO₃. Similar to the disadvantageous addition of CaO, CaCO₃ reacts with sulphuric acid to form CaSO₄, hence intrinsically increasing the content of water-insoluble material. D1 therefore actively teaches away from the present solution, which forms MgSO₄ instead of CaSO₄, and does not contain any pointer or motivation to change the process of D1 to arrive at the method of claim 1.

The solution is also not to be found in D2, and is not obvious starting from the disclosures of D2. D2 teaches the use of potassium hydrogen sulfate as fertilizer, and does not suggest to incorporate the mixture obtained in a production process to prepare an NK or PK fertilizer, so a skilled person trying to solve the problem solved by claim 1 would not look at D2 because it is not related to the same field. Even if a skilled person would look at D2 (*quod non*), he would not find any hint to the technical problem to be solved as D2 is not concerned with the content of water-insoluble material in the final product.

The solution is also not to be found in D3, and is not obvious starting from the disclosures of D3. D3 does not refer to the content of water-insoluble material in a NPK fertilizer. In fact, D3 does not disclose a method to produce a NPK fertilizer, but discloses a method to produce a potassium magnesium sulfate fertilizer material. So a skilled person would not look at D3 when trying to solve the technical problem.

The solution is also not to be found in D4, and is not obvious starting from the disclosures of D4. D4 discloses a method wherein dried sewage sludge is mixed with potassium chloride, phosphoric acid and sulfuric acid. D4 does not refer to water-insoluble components and does not disclose the addition of magnesium oxide to a mixture of potassium sulfate and sulfuric acid.

The solution is also not to be found in D5, and is not obvious starting from the disclosures of D5. D5 discloses a method to produce, and separately recover, potassium magnesium sulfate and magnesium chloride. Again, D5 does not suggest to use its final product to prepare an NP or a PK fertilizer. Hence, a skilled person trying to solve the problem solved by claim 1 would not look at D5 because it is not related to the same field.

The solution is also not to be found in D6, and is not obvious starting from the disclosures of D6. D6 does not refer to the content of water-insoluble material in a NPK fertilizer. In fact, D6 does not disclose a method to produce a NPK fertilizer, but discloses a method to produce a potassium magnesium sulfate fertilizer material. So a skilled person would not look at D6 when trying to solve the technical problem.

Summarized, there is *a priori* no reason why the skilled person would consult D1-D6 to arrive at the solution of the present invention. **Claim 1** of the present application is therefore inventive under Art. 33(3) PCT in view of D1-D6.

Similar considerations apply *mutatis mutandis* to the subject matter of **present claims 2-10, and 12**, which is likewise inventive under Art. 33(3) PCT, in view of the cited prior art, because of the direct or indirect dependency of claims 2-10, and 12 to inventive claim 1.

Present independent **claim 11** differs from D1 in that it refers to a *composition comprising potassium sulphate and magnesium sulphate* to produce a solid, particulate composition, in particular a solid, particulate NPK composition; and wherein a 10 wt% aqueous solution of the composition comprising potassium sulphate and magnesium sulphate has a pH from 3.5 to 4.5, in particular from 3.7 to 4.2.

It is highlighted in the present application on page 5 line 15-17 that the technical effect associated with a pH around 4 for (a neutralized) potassium sulphate composition was that it was found to be very good for producing fertilizer products, in particular NPK fertilizer products.

None of the cited documents D1-D6 refer to a pH sub-range, nor specify a preferred sub-range. Hence, none of the documents D1-D6 hint or suggest to use said composition to produce a solid, particulate composition, let alone a NPK composition.

Summarized, there is *a priori* no reason why the skilled person would consult D1-D6 to arrive at the subject matter of present claim 11. Present claim 11 is therefore inventive under Art. 33(3) PCT in view of D1-D6.

4. Requests

The Applicant respectfully submits that the pending claims fulfill the requirements of the PCT and favorable reconsideration of this application is requested.

Should the International Preliminary Examination Authority not agree, or should a negative statement be considered, the above argumentation notwithstanding, an additional opportunity for submitting arguments and/or amendments is requested under Rule 66.4(b) PCT.

In that case, it is preferred that the matter is settled in an interview, either by telephone, or by videoconference.

The observations contained in the present letter, are made solely for the purposes of the prosecution of this International patent application and without prejudice of the Applicant to National or regional jurisdictions.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'K. Pappaert', with a stylized flourish above it.

Mr. Kris Pappaert
Ms. Lieve Coenegrachts
Professional representatives before the European Patent Office

Encl.: Amended claims, version showing amendments and retyped version

Claims (retyped version)

1. A method for producing a solid, particulate composition comprising from 0 to 2.0 weight% of water-insoluble material, the method comprising the steps of:
 - 5 a) mixing potassium (K) chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid;
 - b) adding magnesium oxide to the composition obtained in step a), such that the magnesium oxide reacts with the sulphuric acid present in the composition produced in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a);
 - 10 c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or phosphorus (P);
 - d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition.
- 15 2. The method according to claim 1, wherein the pH of a 10 wt% aqueous solution of the composition obtained in step b) is from 3.5 to 4.5, in particular from 3.7 to 4.2.
3. The method according to claim 1 or 2, wherein, in step b), from 15 to 25 kg of magnesium oxide per ton of composition obtained in step a) is added to the composition obtained in step a).
- 20 4. The method according to any one of claims 1 to 3, wherein the water content of the composition obtained in step b) is from 0.05 to 0.5 weight%, in particular from 0.05 to 0.23 weight%.
5. The method according to any one of claims 1 to 4, wherein the solid, particulate composition obtained in step d) is a solid, particulate fertilizer composition, in particular a solid, particulate NK, PK, or NPK fertilizer composition.
- 25 6. The method according to any one of claims 1 to 5, wherein step d) is performed in a prilling tower, a drum granulator, a spherodizer, or a fluidized bed granulator.

7. The method according to any one of claims 1 to 6, wherein the composition comprising nitrogen and/or phosphorus further comprises a secondary nutrient and/or a micronutrient.
- 5 8. The method according to any one of claims 1 to 7, further comprising the step of adding a secondary nutrient and/or a micronutrient during step c); or to the composition obtained in step c).
- 10 9. The method according to any one of claims 1 to 8, wherein the composition comprising nitrogen (N) and/or phosphorus (P) used in step c) is obtained by mixing an acidic composition comprising a component selected from the group consisting of nitric acid, sulphuric acid, phosphoric acid, and mixtures thereof, with ammonia.
- 15 10. The method according to any one of claims 1 to 9, further comprising the step of applying a coating composition to the solid, particulate composition obtained in step d).
- 20 11. The use of a composition comprising potassium sulphate and magnesium sulphate to produce a solid, particulate composition, in particular a solid, particulate NPK composition; and wherein a 10 wt% aqueous solution of the composition comprising potassium sulphate and magnesium sulphate has a pH from 3.5 to 4.5, in particular from 3.7 to 4.2.
12. The use of the solid, particulate composition obtained by the method according to any one of claims 1 to 9 as a fertilizer, in particular in fertigation.

Bitte beachten Sie, dass angeführte Nichtpatentliteratur (wie z. B. wissenschaftliche oder technische Dokumente) je nach geltendem Recht dem Urheberrechtsschutz und/oder anderen Schutzarten für schriftliche Werke unterliegen könnte. Die Vervielfältigung urheberrechtlich geschützter Texte, ihre Verwendung in anderen elektronischen oder gedruckten Publikationen und ihre Weitergabe an Dritte ist ohne ausdrückliche Zustimmung des Rechtsinhabers nicht gestattet.

Veuillez noter que les ouvrages de la littérature non-brevets qui sont cités, par exemple les documents scientifiques ou techniques, etc., peuvent être protégés par des droits d'auteur et/ou toute autre protection des écrits prévue par les législations applicables. Les textes ainsi protégés ne peuvent être reproduits ni utilisés dans d'autres publications électroniques ou imprimées, ni rediffusés sans l'autorisation expresse du titulaire du droit d'auteur.

Please be aware that cited works of non-patent literature such as scientific or technical documents or the like may be subject to copyright protection and/or any other protection of written works as appropriate based on applicable laws. Copyrighted texts may not be copied or used in other electronic or printed publications or re-distributed without the express permission of the copyright holder.

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

De Clercq & Partners
Edgard Gevaertdreef 10a
9830 Sint-Martens-Latem
BELGIQUE

PCT

WRITTEN OPINION OF THE INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rule 66)

Date of mailing
(day/month/year)

14.09.2023

Applicant's or agent's file reference
YARA-236-PCT

REPLY DUE
within 2 month(s) from the above date of mailing

International application No.
PCT/EP2022/078604

International filing date (day/month/year)
14.10.2022

Priority date (day/month/year)
15.10.2021

International Patent Classification (IPC) or both national classification and IPC
INV. C05D1/02

Applicant
Yara International ASA

1. ☒ The written opinion established by the International Searching Authority:
☒ is ☐ is not
considered to be a written opinion of the International Preliminary Examining Authority.
2. This second opinion contains indications relating to the following items:
☒ Box No. I Basis of the opinion
☐ Box No. II Priority
☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐ Box No. IV Lack of unity of invention
☒ Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐ Box No. VI Certain documents cited
☒ Box No. VII Certain defects in the international application
☒ Box No. VIII Certain observations on the international application
3. The applicant is hereby **invited to reply** to this opinion.
When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(e).
How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 55.3 and 66.8.
Also: For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4bis. For an informal communication with the examiner, see Rule 66.6. For an additional opportunity to submit amendments, see Rule 66.4.
If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
4. The final date by which the international preliminary report on patentability (Chapter II of the PCT) must be established according to Rule 69.2 is: 15.02.2024

Name and mailing address of the international
preliminary examining authority:

 European Patent Office Gitschiner Str. 103
D-10958 Berlin
Tel. +49 30 25901 - 0
Fax: +49 30 25901 - 840

Authorized Officer

Rodriguez Fontao, M

Telephone No. +31 70 340-3758



Box No. I Basis of the opinion

1. With regard to the **language** , this opinion has been established on the basis of:
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into ,
which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3(a) and 23.1(b)).
 - ☐ publication of the international application (under Rule 12.4(a))
 - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))
2. With regard to the elements of the international application, this opinion has been established on the basis of
(*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"*):

Description, Pages

1-10 as originally filed

Claims, Numbers

1-12 filed in electronic form on

07-07-2023

- ☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
4. ☐ This opinion has been established as if (some of) the amendments listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
5. ☐ This opinion has been established:
- ☐ taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 66.1(d-bis)).
 - ☐ without taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 66.4bis).
6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this opinion (Rule 45bis.8(b) and (c)).

Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	No:	Claims
Inventive step (IS)	No:	Claims 1-12
Industrial applicability (IA)	No:	Claims

2. Citations and explanations:

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1 Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

D1 GB 828 883 A (CHARLES HENRY JOURDAN) 24 February 1960 (1960-02-24)

D2 DATABASE WPI Week 201948 Thomson Scientific, London, GB; AN 2019-39387K XP002806124, & CN 109 650 947 A (CAO H) 19 April 2019 (2019-04-19)

D3 US 7 780 941 B1 (LALANCETTE JEAN-MARC [CA] ET AL) 24 August 2010 (2010-08-24)

D4 DATABASE WPI Week 197546 Thomson Scientific, London, GB; AN 1975-76416W & JP S50 68857 A (HIKARI IND KK) 9 June 1975 (1975-06-09)

D5 DATABASE WPI Week 199911 Thomson Scientific, London, GB; AN 1999-121795 & CN 1 197 039 A (ZHANG Z) 28 October 1998 (1998-10-28)

D6 DATABASE WPI Week 201525 Thomson Scientific, London, B; AN 2015-18845V & CN 104 311 164 A (LOMON LAND AGRIC CO LTD) 28 January 2015 (2015-01-28)

2 INDEPENDENT CLAIM 1

The present application does not satisfy the requirements set forth in Article 33(3) PCT because the subject matter of claim 1 does not involve an inventive step in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

2.1 D1 is considered to be the closest prior art. This document describes a method comprising the steps of:

- a) mixing potassium (K) chloride and sulphuric acid, thereby producing a composition comprising potassium sulphate and sulphuric acid;
- b) adding dolomite to the composition obtained in step a), thereby neutralizing the sulphuric acid comprised in the composition obtained in step a);

- c) adding the composition obtained in step b) to a composition comprising nitrogen (N) and/or phosphorus (P);
d) solidifying the composition obtained in step c), thereby producing a solid, particulate composition (see claims 1,2,4,6; examples 4,5,7).
- 2.2 The difference between the subject-matter of claim 1 and the teaching of D1 lies in the fact that magnesium oxide is added to the composition obtained in step a) whereas in D1 dolomite is used.
- 2.3 The technical effect mentioned by the applicant in the description in relation to the use of magnesium oxide instead of calcium oxide lies in the fact that magnesium sulphate is formed which has a better solubility than calcium sulphate.
- 2.4 In this context, the problem to be solved in view of D1 can be considered as the provision of a potassium sulphate containing fertiliser obtained by the reaction and further neutralization of sulphuric acid with potassium chloride with improved solubility.
- 2.5 Departing from D1 the skilled person would be aware that the neutralization with calcium containing materials such as dolomite would lead to the formation of calcium sulphate in addition to magnesium sulphate. The problem of the solubility of a fertiliser composition is well known to the skilled person that would be prompted to look for soluble fertiliser alternatives if the final product is going to be used in fertigation.
- 2.6 In this sense, using magnesium oxide in order to neutralise an acidic potassium sulphate mixture obtained by the reaction of sulphuric acid with potassium chloride, is a measure that the skilled person would apply without the exercise of an inventive skill, specially since these features have already been employed for the same purpose in a similar method (see D1 paragraphs [0009]-[0011]) and where the same result is to be achieved.
- 2.7 It would, therefore, be obvious to the person skilled in the art, namely when the same result is to be achieved, to apply these features with corresponding effect to the method according to D1, thereby arriving to the method according to claim 1.
- 2.8 The same applies in view of the combination of D1 with documents D3 (see claims 1,8,9) and D4, D5, D6 (see respective abstracts).
- 2.9 It is therefore considered that the subject-matter of claim 1 lacks an inventive step in the sense of Article 33(3) PCT.

3 DEPENDENT CLAIMS 2-10

Dependent claims 2-10 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect inventive step (Article 33(3) PCT). The subject-matter of these claims is either known from the combination of documents or considered to be common practice for a man skilled in the art.

3.1 The subject-matter of claims 2-6 is known from document D1 (see claims; examples 4,5,7) and lacks therefore an inventive step following the same reasoning used above for the subject-matter of claim 1.

3.2 The subject-matter of claims 7-10 is considered to be mere embodiments within the ambit of claim 1 from which they depend. The technical features of said claims have not been shown to substantiate to a technical effect in a non-obvious manner nor a problem has been shown to have been solved by the application of these features. The technical features of this claims are considered as normal practice in the fertiliser field.

4 INDEPENDENT CLAIM 11

Notwithstanding, the observations made below under Item VIII, the present application does not satisfy the requirements set forth in Article 33(3) PCT because the subject matter of claim 1 does not involve an inventive step in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

4.1 The same reasoning used above for the subject-matter of claims 1 and 2 applies here, mutatis mutandis.

5 INDEPENDENT CLAIM 12

5.1 The present application does not satisfy the requirements set forth in Article 33(3) PCT because the subject matter of claim 12 does not involve an inventive step in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT), departing from D1 and following the same reasoning used above for the subject-matter of claim 1.

Re Item VII

Certain defects in the international application

6 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in D1-D6 is not mentioned in the description, nor are these documents identified therein.

Re Item VIII

Certain observations on the international application

- 7 The application does not meet the requirements of Article 6 PCT, because claims 1 and 11 are not clear.
- 7.1 There is a discrepancy between the technical features mentioned in the drafting of independent claims 1 and 11 in the following sense:
- The compositions corresponding, respectively, to the method described in claim 1, and to the use described in claim 11, do not have the same scope, since there is no limitation imposed on the water solubility of the composition in claim 11 nor to the pH of the aqueous solution of the composition in claim 1.
- The present drafting of claims 1 and 11 tends therefore to cast uncertainty as to which are the technical features essential for carrying out the invention and which are the technical features which can be considered as further features relating to different embodiments of the present application.
- 7.2 Furthermore, since solid, particulate compositions comprising potassium sulphate and magnesium sulphate are known in the art, these claims at least formally do not meet the requirements of unity of invention.
- 7.3 Claim 1 also do not meet the requirements of Article 6 PCT because the matter for which protection is sought is not clearly defined. The passage "comprising from 0 to 2.0 weight% of water-insoluble material" attempts to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

0	For International Preliminary Examining Authority use only	
0-1	Identification of IPEA	
0-2	Date of receipt of DEMAND	
0-3	Form - PCT/IPEA/401 PCT Demand	
0-3-1	Prepared Using	eOLF Version: FMMNGR5183, IBR4015182, FM_FOP0205
0-4	Demand under Article 31 of the Patent Cooperation Treaty: The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).	
0-5	International Preliminary Examining Authority (specified by the applicant)	IPEA/EP
I	Identification of the International application	
I-1	International Application No.	PCT/EP2022/078604
I-2	International Filing Date	14 October 2022 (14.10.2022)
I-3	(Earliest) Priority Date	15 October 2021 (15.10.2021)
I-4	Applicant's or agent's file reference	YARA-236-PCT
I-5	Title of Invention	Method for producing a potassium-containing fertilizer with a low content of water-insoluble material

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

II-1	Applicant	
II-1-1	Name	YARA INTERNATIONAL ASA
II-1-2	Address	Drammensveien 131 0277 Oslo Norway
II-1-3	State of nationality	NO
II-1-4	State of residence	NO
II-1-5	Telephone No.	
II-1-6	e-mail	
II-1-7	Applicant's registration No. with the Office	
III-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	Attorney (appointed earlier)
III-1-1	Name	De Clercq & Partners
III-1-2	Address	Edgard Gevaertdreef 10a 9830 Sint-Martens-Latem Belgium
III-1-3	Telephone No.	+3292802340
III-1-4	e-mail	info@dcp-ip.com
III-1-4a	The International Preliminary Examining Authority is authorised to use this e-mail address, if the Authority so wishes, to send notifications issued in respect of this international preliminary examination:	exclusively in electronic form (no paper notifications will be sent)
III-1-5	Agent's registration No.	458

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

IV	Basis for International Preliminary Examination			
IV-1-1	Statement concerning amendments: The applicant wishes the International Preliminary Examination to start on the basis of:	-the description as originally filed -the claims as amended under Article 34 -the drawings as originally filed		
IV-2	Language for the purposes of international preliminary examination:	English -(which is the language in which the international application was filed)		
V	Election of States	The filing of this demand constitutes the election of all Contracting States which are designated and are bound by Chapter II of the PCT.		
VI	Check list	Number of sheets	Electronic file(s) attached	Received Y/N (For IPEA use only)
	The demand is accompanied by the following elements, in the language referred to under item IV-2 for the purposes of international preliminary examination:			
VI-2 (1)	Amendments under Art. 34	2	AMDA34-1.pdf	
VI-6	Letter accompanying the amendments under Article 34 (Rule 66.8)	6	LETT.pdf	
VI-7	Other: Other document	2	OTHERDOC-1	
	Accompanying Items	Details	Electronic file(s) attached	Received Y/N (For IPEA use only)
	The demand is also accompanied by the following item(s):			
VI-8	Fee calculation sheet	1	fees.pdf	
VII-1	Signature of applicant, agent or common representative	PKCS7 Digital Signature: Kris Pappaert 28134		
VII-1-1	Name	De Clercq & Partners		
VII-1-2	Capacity	Representative		
VIII	Note(s) to IPEA/EP			

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

FOR INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY USE ONLY

8-1	Date of actual receipt of DEMAND	
8-2	Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b)	
8-3	The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and items 8-4 and 8-5 below do not apply.	
8-3-1	The applicant has been informed accordingly	
8-4	The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.	
8-5	Although the date of receipt of the demand is after the expiration of the 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.	
8-6	The date of receipt of the demand is AFTER the expiration of the time limit under Rule 54bis, 1(a) and item 7 or 8, below, does not apply.	
8-7	The date of receipt of the demand is WITHIN the time limit under Rule 54bis.1(a) as extended by virtue of Rule 80.5.	
8-8	Although the date of receipt of the demand is after the expiration of the time limit under Rule 54bis.1(a), the delay in arrival is EXCUSED pursuant to Rule 82.	

FOR INTERNATIONAL BUREAU USE ONLY

9-1	Demand received from IPEA on	
-----	------------------------------	--

© WPI / 2017 Clarivate Analytics.

AB - Fertilisers are produced from sewage sludge. In an example, dried sewage sludge 75 pts was mixed with KCl 9 pts. The sludge mixt. was kneaded with a mixt. contg. 53% H₃PO₄ and 70% H₂SO₄ 10 pts.

AN - 1975-76416W

AP - JP19730112263 19731008

CPY - HIKA-N

DC - C04 D16

DW - 197546; 198205

ICAI - C05F7/00

IW - FERTILISER PREPARATION SEWAGE SLUDGE MIX DRY POTASSIUM CHLORIDE MIXTURE PHOSPHORIC SULPHURIC ACID

IWW - FERTILISER PREPARATION SEWAGE SLUDGE MIX DRY POTASSIUM CHLORIDE MIXTURE PHOSPHORIC SULPHURIC ACID

M1 - [01] M423 M431 M782 M902 P113 R003 V600 V632 V633

M2 - [02] C101 C108 C316 C540 C730 C800 C801 C802 C804 C805 M411 M431 M782 M902 P111 P112 R003
- [03] B115 B701 B713 B720 B815 B819 B831 C101 C108 C800 C802 C804 C805 C807 M411 M431 M782 M902 P111 P112 R003
- [04] A119 A940 C017 C100 C730 C801 C803 C804 C805 C806 C807 M411 M431 M782 M902 P111 P112 R003
- [05] C101 C108 C316 C540 C730 C800 C801 C802 C804 C805 M411 M431 M782 M903 P111 P112 R003 R044 R045 R046 R047
- [06] B115 B701 B713 B720 B815 B819 B831 C101 C108 C800 C802 C804 C805 C807 M411 M431 M782 M903 P111 P112 R003 R044 R045 R046 R047
- [07] A119 A940 A990 C000 C017 C100 C730 C801 C803 C804 C805 C806 C807 M411 M431 M782 M903 P111 P112 R003 R044 R045 R046 R047

MC - C04-B04B C05-A01A C05-B02A5 C05-C05 C12-N09 C12-N10 D04-B01

NC - 1

NPN - 2

OPD - 1973-10-08

PA - (HIKA-N) HIKARI IND KK

PAW - (HIKA-N) HIKARI IND KK

PD - 1975-06-09

PN - JPS5068857 A 19750609 DW197546
JPS5715188 B 19820111 DW198205

PR - JP19730112263 19731008

TI - Fertilisers prep'd. from sewage sludge - e.g. by mixing dried sludge with potassium chloride then with mixt. of phosphoric and sulphuric acids

UPA - 20130325

UPM -

JPS5068857A 19750609

EPO

SUBJECT OF THE INVENTION

Manufacture of fertilizer

[0001] 'tll-' 20 Inventor Morishitati Rin Name Morishita Gozo (2 others) 3 Applicant Taka 2 Deyo Address 1-5-5 Takaracho, Chuo-cho, Tokyo 4, Agent Gosho Shiba-Daimon-Minato-ku, Tokyo No.9! J50 Japan Patent Office Kabuto JP 50-slas 70 Publication date 50. (1975) 6.9 ■ Japanese Patent Application No. 48-1122 O3 Agency reference number 73 / 4 ϕ Specification 1, Invention of the invention Name 2, Claim B: When organic wastewater is treated by the activated sludge method, a mineral acid is added to excess sludge produced as a by-product, and nitrogen sludge and phosphorus asperity contained in the excess sludge are dissolved in water. Manufacture of fertilizer.

[0002] 3. Detailed Description of the Invention The present invention relates to a method for producing fertilizer, and more particularly to a method for producing fertilizer from wire mesh sludge which is produced when organic waste liquid is treated by an activated sludge method. In the field of public wastewater treatment such as municipal sewage, the so-called activated sludge method utilizing the biochemical reaction of microorganisms has been widely used. As the problem of closeness is closed, the lifting method will be adopted in the fields of petrochemical industry, chemical manufacturing, sugar manufacturing, fermentation industry, leather processing, food manufacturing, etc. □ Water treatment in various industries. There are many factories that are developing. Excess sludge is produced as a by-product in the process of treating organic "waste liquid" by the activated sludge method. However, conventional treatment of municipal water generally has a relatively low BOD load and a small amount of excess sludge. For example, in the case of waste liquid treatment in the petrochemical industry and the like, the BOD load is high and the treatment scale is very large, so that a large amount of excess sludge is generated, and the treatment is becoming a serious problem. As a method of treating excess sludge, which has been performed in the field of municipal sewage treatment and the like, a method of disposing (landfilling) after drying with a flash dryer, a rotary kill / etc. Although it is used, the secondary pollution caused by disposal and incineration of dried sludge has various problems in terms of maintenance and management of the equipment, economic efficiency, etc. I mean, It is very difficult to apply this method to large-scale wastewater treatment such as industrial wastewater treatment, etc. On the other hand, the chemical properties of the excess sludge, namely, various EndPage: 1 cell protein as a main component, and various tamino acids , Rich in vitamins, nitrogen, acid, potash, lime, etc. The amount of fertilizing ingredients is similar to conventional

organic "fertilizer, such as rapeseed oil cake, fish cake, etc. Attempts to use this excess sludge as an 'organic fertilizer' have been made to replace the surplus sludge, and in one part only one L1 that has already been gagged, according to the findings of the present inventors, When the surplus sludge is applied alone as fertilizer, the elution of fertilizer component into the soil is slow, and all the components are not always fully utilized. As a result, there is a defect that the initial growth of the crop is delayed. (1) The present inventor has found a problem in using excess sludge as fertilizer. As a result of repeated examinations, the cause of the above-mentioned slow-acting properties is that bacteria, filamentous fungi, algae, protozoa and rotifers, etc. Zuirea bacteria whose cell membrane is mainly coated with neutral sugars and glycopeptides whose main components are xoseamine and cyanic acid, etc. ; E, R difficulty == changed to dura matter, and □ ね 6. 0. , When mineral acid is added to the mud, the hardening of the glycopeptide is degraded and the protein components inside the cells are also degraded at the same time. The present inventors have found out that the nitrogen component and the batter component can be easily turned into a sluice, and have completed the present invention. In the case where one part organic waste liquid is treated by the activated sludge method, it is generally used as a coagulant for facilitating the pH adjustment of the waste liquid to be treated, the sedimentation and separation of nutrients for propagation of microorganisms or excess sludge. Significant amounts of calcium compounds, phosphates, ammonia and iron compounds, etc., are added, which often form sparingly soluble salts, such as distillers, iron phosphate, aluminum phosphate, phosphorus-tricalcium lime, and "surplus" However, according to the method of the present invention, the effect of II on the easily soluble salt 1 of these hardly soluble salts is remarkably improved according to the method of the present invention. The type of the mineral acid to be used in the present invention is not particularly limited. In principle, any type may be used without limitation. Usually, sulfuric acid, hydrochloric acid, nitric acid or phosphoric acid is used. However, speaking of general trends, sulfuric acid is the most effective Then, the effect decreases slightly in the order of hydrochloric acid, nitric acid and phosphoric acid. On the other hand, nitric acid and phosphoric acid, on the other hand, are themselves preferable as fertilizers, and are preferable from the viewpoint of utilization as fertilizers, and are not always uniform. Similarly, there is no strict restriction on the amount of used shield. For example, by adjusting the amount, it is possible to adjust the slow-release effect and the degree of the fertilizer, and furthermore, there is a large excess of minerals in excess sludge. Alkali components such as phylum ammo-a and potassium added with acid. The compound fertilizer with diammonium salt, potassium salt or the like can be used by neutralizing with-, and can be appropriately selected depending on the purpose. In carrying out the method of the present invention, the excess sludge is used alone as a fast-acting fertilizer. It is sufficient to simply add and mix the mineral acid. Further, as an application of the present invention, after mixing the powdery potassium raw material or the magnesia raw material with the dried granular excess sludge, the mineral acid is added or the third acid is added to the mineral acid. Ingredients. By mixing and stirring the dissolved and dispersed solution, it can be easily granulated to form a simple fertilizer with a

simple fertilizer and a sufficient amount of fertilizer for the type of crop and its growth. A complete four-composite fertilizer i having a desired component composition. Hereinafter, the present invention will be described more specifically with reference to examples. In the examples, all percentages are based on weight. Example 1 Total nitrogen (TN) content 8,000%, water-soluble nitrogen, elemental (wN) content 0.11%, kama phosphoric acid (T-'p) content 3.80%, Water-soluble phosphoric acid (w-p) content 0.20%,)). EmMiK sulfuric acid. (7% aqueous solution), hydrochloric acid (32% certain solution), nitric acid (65% aqueous solution), phosphoric acid- (73% aqueous solution) EndPage: 2 The ratios of -N and WP are shown below. {Use ratio% Fertilizer adulteration female water solubility% treatment activated sludge mineral acid WN, WP, N, P2O sulfuric acid 201, 131, 821.6. 557.680 diacid 200.80.11.5711.32'8. -180 nitric acid 2.03.530.77, 9.0'21.280 hydrochloric acid 200.690.8699.524.382 sulfuric acid 181.13'1.5116.145. j87 sulfuric acid 11G, 991.44'13.040.487 cynic acid 1'30.7's7. s39.2.2.4.587 nitric acid 1a2.51.6.82'7.920.7787 hydrochloric acid 130.75'0.899.5j'22i'9939nba'IO ,, 36,3,9j, 3 . i5. j Example 2 JP-A-50-68857 (1) Granular dry sludge 75 with T-N 8.0.0%, W-NO, 1.1%, T = p 3.8%, W-Po, 20% Parts and 9 parts of 60.00% chloride potassium added to W-, and 6 parts and 7 parts of 53.0.0% WP phosphoric acid separately. A mixture of 0% sulfuric acid 1' 0 parts in advance was added and kneaded. T-N 6.05%, WN' 0. 7' 6%, T-P5.9. A complete compound fertilizer containing '9%, WP 4.20% and W-K 6.1.0% was obtained. At this time, the water solubility was 1% Ni and 31% P. Attorney Seiki Kikuchi-5, Catalog of the attached documents 1) One copy of the description 2) One copy of the application 3) One copy of the power of attorney 6, other inventor Ni ss i aso! " "Address 1.916 Nishi Yuma, Omiya City, Saitama Prefecture Full name fM rhinoceros Address: 8-8-13 VW 2-chome, Nakano-ku, Tokyo 1) Shigeyuki EndPage: 3

CN1197039A 19981028

IPPH

SUBJECT OF THE INVENTION

Single stage method is produced the method for agricultural potassium sulfate

- [0001] The invention belongs to chemical technology field, is a kind of method of producing agricultural potassium sulfate.
- [0002] Agriculture production needs a large amount of potash fertilizer, and producing vitriolate of tartar at present has natural mineral preparing process and conversion method, the 56th page of production method of having introduced vitriolate of tartar of " chemical engineer " 1/1996 (total the 52nd phase).Conversion method mainly contains Mannheim proeess to be the hot method of representative and to be the wet method of representative with the double decomposition.Mannheim proeess mature production technology, flow process weak point, Repone K transformation efficiency height, constant product quality, shortcoming is that equipment corrosion is serious, and the reaction in furnace temperature is up to 600-700 , and temperature of combustion reaches 1000-1400 , separate unit throughput is low, maintenance load, investment cost height.The energy consumption of double decomposition is lower, and is pollution-free, but double salt can not decompose fully, and the quality product utmost point is waited to improve.
- [0003] The objective of the invention is to provide the method for the step production agricultural potassium sulfate that a kind of transformation time is short, transformation efficiency is high, energy consumption is low, temperature of reaction is low.
- [0004] Production method of the present invention is: put into 25 -35 warm water in reactor, adding Repone K starts agitator and constantly stirs, form saturated warm turbid liquid, add the vitriol oil again, constantly stir and react with Repone K, reaction times is 70-180 minute, add magnesia powder at last, stir and stop after 15-25 minute stirring, the hydrogenchloride that is generated is drawn out of and can be made into the byproduct magnesium chloride, reaction solution is cooled to 25-30 to going into cooling pool from still, can obtain solid-state vitriolate of tartar and mother liquor through the whizzer separation, can get byproduct potassic-magnesian fertilizer, wherein sulfuric acid behind the mother liquid evaporation, Repone K, magnesium oxide, the weight percent of water is: sulfuric acid: 26.2-28.4%; Repone K: 39.6-42%; Magnesium oxide: 0.019-0.27; Water: 34%-29.33%.

- [0005] The present invention can adopt finish production simple one step of equipment, and transformation time is short, and wherein the still internal reaction needs 5-7 hour, finishes the full scale production process in 12-14 hour, and energy consumption is low, and temperature of reaction is low, and top temperature is no more than 100 in the still, and Repone K can be transformed fully.
- [0006] Below provide three embodiment of the present invention:
- [0007] Example one:
- [0008] (1) 60 kg of water are heated to 30 , inject still, start agitator then, add 85.6 kilograms of Repone K simultaneously, because its heat absorption, temperature is reduced to 15 in the still at this moment, and whole process is wanted half an hour;
- [0009] (2) speed with 5 kilograms of per minute injections adds 56.3 kilograms of sulfuric acid, in still, react with Repone K, and stable for some time, whole process 72 minutes;
- [0010] (3) add 5.82 kilograms of magnesia powders, react 20 public clocks, and close agitator, go out still;
- [0011] (4) open-air water-cooled is 5 hours, and temperature is reduced to 25 , through whizzer, and 80 kilograms of vitriolate of tartar of output and 33.82Kg potassic-magnesian fertilizer.
- [0012] Example two:
- [0013] (1) 300 kg of water are heated to 27 , inject still, start agitator, add 342.4 kilograms of Repone K simultaneously, because of heat absorption, temperature is reduced to 12 , and at this moment process is wanted half an hour;
- [0014] (2) speed of 5 kilograms of per minutes adds 225.2 kilograms of vitriol oils, in still, react with Repone K, and whole process of stable for some time 105 minutes;
- [0015] (3) add 17.46 kilograms of magnesia powders, reacted 20 minutes, and close agitator, go out still;
- [0016] (4) open-air water-cooled is 6.5 hours, and temperature is reduced to 30 , through whizzer, and 320 kilograms of vitriolate of tartar of output and 121.46 kilograms of potassic-magnesian fertilizers.
- [0017] Example three:

- [0018] (1) 700 kg of water are heated to 25 , inject still, start agitator, add 856 kilograms of Repone K simultaneously, because of its heat absorption, temperature is reduced to 12 , this process need half an hour;
- [0019] (2) speed with 5 kilograms of per minutes adds 563 kilograms of vitriol oils, in still, react with Repone K, and stable for some time, whole process is wanted 180 minutes;
- [0020] (3) add 40.73 kilograms of magnesia powders, reacted 20 minutes; Close agitator, go out still;
- [0021] (4) open-air water-cooled is 7 hours, and temperature is reduced to 30 ; Through whizzer, 800 kilograms of vitriolate of tartar of output and 296.74 kilograms of potassic-magnesian fertilizers.

A kind of single stage method is produced the method for agricultural potassium sulfate, it is characterized in that in reactor, putting into 25 -35 warm water, add Repone K and stir into saturated turbid liquid, adding sulfuric acid again stirred 70-180 minute, adding magnesium oxide at last stirred 15-25 minute, can obtain vitriolate of tartar through separating when being cooled to 25-30 , wherein the weight percent of raw material is: sulfuric acid: 26.2-28.4%; Repone K: 39.6-42%; Magnesium oxide: 0.019-0.27%; Water: 34%-29.33%.

© WPI / 2017 Clarivate Analytics.

AB - One-step process for preparing potassium sulphate comprises addition of potassium chloride to a reactor containing warm water, stirring, and addition of concentrated sulphuric acid while stirring. After a certain time, magnesium oxide powder is added, the stirring stopped and the mixture cooled to 25-30 degree C. The products are separated to obtain potassium sulphate and by-products (magnesium chloride and potassium-magnesium fertiliser).
- **ADVANTAGE :**
The process requires simple apparatus, a short conversion time (5-7 hours for reaction and 12-14 hours for total process), low consumption of energy and a reaction temperature of lower than 100 degree C.

AN - 1999-121795

AP - CN19971009817 19970423

CPY - ZHAN-I

DC - C04 E34

DW - 199911

ICAI - C05D1/02

IN - ZHANG Z

INW - ZHANG Z

IW - PRODUCE AGRICULTURE POTASSIUM SULPHATE COMPRISE STIR CHLORIDE WARM WATER ADD SULPHURIC ACID MAGNESIUM OXIDE POWDER

IWW - PRODUCE AGRICULTURE POTASSIUM SULPHATE COMPRISE STIR CHLORIDE WARM WATER ADD SULPHURIC ACID MAGNESIUM OXIDE POWDER

LNKA - 1999-035824

MC - C05-A01A C05-C05 E05-A E05-S

NC - 1

NPN - 1

OPD - 1997-04-23

PA - (ZHAN-I) ZHANG Z

PAW - (ZHAN-I) ZHANG Z

PD - 1998-10-28

PN - CN1197039 A 19981028 DW199911

PR - CN19971009817 19970423

TI - Production of agricultural potassium sulphate - comprises stirring potassium chloride in warm water, adding sulphuric acid, then adding magnesium oxide powder

UPA - 20130325

UPM -

CN104311164A 20150128

IPPH

SUBJECT OF THE INVENTION

A kind of production method of potash magnesium sulphate fertilizer

[0001] Technical field**[0002]** The present invention is specifically related to a kind of production method of potash magnesium sulphate fertilizer, belongs to technical field of chemical fertilizer production.**[0003]** Background technology**[0004]** The molecular formula of potash magnesium sulphate fertilizer is $K_2SO_4 \cdot m(MgSO_4) \cdot nH_2O$ (is $m=1 \sim 2$ wherein, $n=0 \sim 6$), it is a kind of inorganic green fertilizer being rich in K, Mg, S tri-kinds of nutrients, water-soluble fabulous, potassium, magnesium and element sulphur can not only be provided to plant and energy chessom, promote growing of the leaf of plant, branch and root system, make root system of plant huge, plant can be impelled simultaneously to accelerate to absorb the element such as Nitrogen In Soils, phosphorus, increase the ability of plant resistant disease. Potassium magnesium sulfate belongs to chemically neutral salt, and use and can not affect P in soil H value, chloride content is low in addition, and the Effects of Salinity of long-term application to soil is less.**[0005]** At the annual amount of application of U.S.'s potash magnesium sulphate fertilizer at hundreds of thousands of ton, also a large amount of for preparing composite fertilizer except directly using, according to soil quality and the crop situation preparation special fertilizer on each farm. New variety of potash fertilizer series are still belonged at Chinese potash magnesium sulphate fertilizer. At present, potash magnesium sulphate fertilizer is worldwide widely used, and 30% of U.S.'s potash magnesium sulphate fertilizer brand " Shi Baomi " ultimate production sells to Mexico, Costa Rica, Colombia, Brazil, Venezuela, Ecuador, Peru, Australia, Japan, Korea S, Philippines, Malaysia, Thailand and some areas, Europe etc. Typically " Shi Baomi " chemical constitution is: $w(K_2O)=22\%$, $w(Mg)=11\%$ and $w(S)=22\%$, its most important proterties is solubility good (100% is water-soluble), but solubleness is slightly lower than Repone K. Another important character of " Shi Baomi " is that its composition is mainly neutral salt, uses and can not affect P in soil H. Because its composition is mainly sulfate radical, chlorine ions mark is lower than 1.5%, and thus its salt index is relatively low. Compared with traditional potassium product, potash magnesium sulphate fertilizer adds magnesium moderate-element, for crop provides nutrient

balanced more comprehensively. Along with China's soil salinization problem is increasingly severe, replace the status of Repone K in agricultural planting gradually without chlorine high-quality potash fertilizer (potassium sulfate and potassium magnesium sulfate).

[0006] The raw material producing potash magnesium sulphate fertilizer in China is Shoenite ore deposit, and molecular formula is $K_2Mg(SO_4)_2 \cdot 6H_2O$ is one of essential mineral of soluble potassium salt mine. The production method of potash magnesium sulphate fertilizer is divided into natural extract method and blending method two kinds according to raw material is different with technique. Natural extract method comprises and adopts salt lake brine or solid kalium-magnesium deposit through physical method direct production and adopt potassium magnesium navajoite direct production two kinds of techniques, shortcoming is larger by raw material supply limitations affect, technical process is comparatively complicated, operation controls inconvenient, and in the operating process of flotation and crystallization, accuracy requirement is higher. And blending method produces with potassium sulfate or Repone K and the simple blending of magnesium salts, the potash magnesium sulphate fertilizer that the method is produced is only the mixture of sulphate of potash and magesium, quality product is uneven, and it with the potassium sulfate of high price for raw material, cost advantage is obviously not enough. And whether the potash magnesium sulphate fertilizer adopting the simple blending mode such as potassium sulfate and magnesium oxide to produce can deserve to be called potash magnesium sulphate fertilizer, and mainly should see its chloride ion content, potassium content should be greater than Mg content simultaneously. But the potassium magnesium sulfate fertilizer product of some blending of selling in the market, although all contain potassium, sulphur, magnesium, some chlorion exceeds standard, and the Mg content of some product is greater than potassium content, and these products all do not reach the specification of quality of potash magnesium sulphate fertilizer.

[0007] Summary of the invention

[0008] Object of the present invention is just, for above-mentioned the deficiencies in the prior art, to provide the production method that a kind of potash magnesium sulphate fertilizer is new, and the method production technique is simple, and raw material sources are extensive, and cheap, production cost is low.

[0009] To achieve these goals, the technical solution used in the present invention is such:

[0010] A kind of production method of potash magnesium sulphate fertilizer, it is characterized in that: it with Repone K, the vitriol oil and magnesium oxide for raw material, Repone K and strong sulfuric acid response obtain sal enixum slip, sal enixum slip obtains potassium magnesium sulfate slip

with magnesium oxide slip again, and namely potassium magnesium sulfate slip obtains potash magnesium sulphate fertilizer through cooling, fragmentation, baking operation.

[0011] Further, the preparation method of above-mentioned potassium magnesium sulfate slip comprises the following steps:

[0012] (1) prepare sal enixum slip: potassium chloride and vitriol oil mix and blend react 30-60min, hydrogen chloride gas is overflowed to obtain sal enixum slip, and wherein control temperature of reaction 80 ~ 140 DEG C, the mol ratio of Repone K and the vitriol oil is with KCl and H₂SO₄count 1:1 ~ 1.2;

[0013] (2) magnesium oxide slip is prepared: according to quality than magnesium oxide: water=1:0.5 ~ 2, magnesium oxide is mixed obtained magnesium oxide slip with water;

[0014] (3) potassium magnesium sulfate slip is prepared: the sal enixum slip obtained by step (1) and the magnesium oxide slip Hybrid Heating of step (2) are reacted 5 ~ 10min and namely obtained potassium magnesium sulfate slip, wherein controlling temperature of reaction is 120 ~ 160 DEG C, and the mol ratio of sal enixum slip and magnesium oxide slip is with KHSO₄1:1 is got with MgO meter.

[0015] Further, in order to promote the reaction of sal enixum, described in step (1), Repone K mixes with the vitriol oil in the form of a solution, wherein concentration >=50% of Klorvess Liquid.

[0016] Equally, in order to sal enixum is produced in accelerated reaction, concentration >=90% of the vitriol oil described in step (1).

[0017] Further, the hydrogen chloride gas grading absorption that described step (1) is overflowed makes hydrochloric acid.

[0018] Compared with prior art, the invention has the advantages that: the present invention is with cheap Repone K, the vitriol oil and magnesium oxide for raw material, and principal reaction equation is:

[0019] $\text{KCl} + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HCl} \uparrow$

[0020] $\text{KHSO}_4 + \text{MgO} + (n-1)\text{H}_2\text{O} = \text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot n\text{H}_2\text{O} \quad (1 \leq n \leq 6)$

[0021] First by Repone K and vitriol oil hybrid reaction, by controlling temperature of reaction at 80 ~ 140 DEG C, obtain sal enixum slip, and hydrogen chloride gas is discharged in gaseous form under the condition of heating, react completely to ensure simultaneously, not chloride ion-containing in the

sal enixum slip generated, the mol ratio of Repone K and the vitriol oil is with KCl and H_2SO_4 count 1:1 ~ 1.2; The hydrogen chloride gas sectional of effusion absorbs makes hydrochloric acid to reach the recycling of waste gas.

- [0022] Then magnesium oxide is mixed obtained magnesium oxide slip with water, with to make in its and sal enixum slip and time be convenient to stir, react completely, by control temperature of reaction 140 ~ 160 DEG C, the mol ratio of sal enixum slip and magnesium oxide slip is with $KHSO_4$ get 1:1 with MgO meter, in magnesium oxide slip and sal enixum slip and completely, obtain potassium magnesium sulfate slip, this potassium magnesium sulfate slip obtains potassium magnesium sulfate fertilizer product through cooling, broken, oven dry.
- [0023] The reaction of Repone K and sulfuric acid is replacement(metathesis)reaction, needs to control range of reaction temperature at 80 ~ 140 DEG C, and guarantee reaction generates purity sal enixum slip up to standard.If temperature is lower than 80 DEG C, it is clean that the hydrogenchloride that reaction generates is difficult to effusion, causes residual chloride hydrogen in sal enixum slip too much, make potassium magnesium sulfate fertilizer product chloride ion content not reach national standard requirement.If temperature is higher than 140 DEG C, the evaporation of reaction process moisture is too fast, needs constantly to supplement clear water to reaction vessel, causes sal enixum slip mobility variations large, be unfavorable for the control to reaction process, and the unit consumption of energy that control temperature crosses high product will increase considerably.The speed of reaction of Repone K and sulfuric acid is moderate, and the reaction times controls at 30-60min, can ensure to react completely.
- [0024] Sal enixum and magnesian reaction are neutralization reaction, and temperature range controls at 120 ~ 160 DEG C, ensure that neutralization obtains potassium magnesium sulfate slip.If temperature is lower than 120 DEG C, rapid crystallization solidifies by the potassium magnesium sulfate slip that reaction generates, and affects residual sulfuric acid hydrogen potassium and magnesian continuation reaction.If temperature is higher than 160 DEG C, the evaporation of reaction process water is too fast, and potassium magnesium sulfate slip mobility will significantly reduce, and will affect sal enixum and magnesian abundant reaction equally.When temperature is lower than 120 DEG C or higher than 160 DEG C, all may make sal enixum and magnesium oxide can not complete reaction, cause content of magnesia in product too high, make product water insolubles content not reach national standard requirement.In addition, for ensuring that magnesium oxide and sal enixum can fully react, magnesium oxide should in advance according to quality than magnesium oxide: water=1:0.5 ~ 2 are mixed with slip, and the water yield added just in time can meet the needs of potassium magnesium sulfate crystal water and maintenance product adequate liquidity.If magnesium oxide: water # 1:2, the potassium magnesium sulfate slip mobility extreme difference of generation, is unfavorable for fully carrying out of reaction, insoluble content of magnesia in product is exceeded standard.If magnesium oxide: water # 1:0.5,

the potassium magnesium sulfate water content that reaction is produced is too high, can not be directly broken after naturally cooling, and will increase the oven dry cost of product. Sal enixum and magnesian speed of reaction high, the reaction times controls at 5-10min, can ensure to react completely.

[0025] The preparation method of potash magnesium sulphate fertilizer provided by the present invention, with Repone K, magnesium oxide and sulfuric acid for raw material, Commercial sources is extensive, and product yield can reach 99%, and production cost is lower.

[0026] The present invention adopts potassium chloride low-temperature conversion method production technique, raw material adopts and adds by formula in batches, technical process is briefly easily controlled, and can ensure the quality of product completely, and the potash magnesium sulphate fertilizer obtained taste can meet or exceed national potash magnesium sulphate fertilizer acceptable end product standard (GB/20937-2007).

[0027] Embodiment

[0028] In order to the object of the present invention of understanding clearly, technical scheme and beneficial effect, below the present invention is described further, but not by protection scope of the present invention limit in the examples below.

[0029] Potash magnesium sulphate fertilizer product standard GB/T20937-2007 is applicable to only through the potassium magnesium sulfate fertilizer product containing the moderate-element such as magnesium, sulphur that physical method extracts or direct removing impurity is made from salt lake brine or solid kalium-magnesium deposit, and its standard content is as shown in the table:

[0030] [image]

[0031] Embodiment 1:

[0032] (1) sal enixum slip is prepared:

[0033] The 108.9Kg vitriol oil (H is added in reactor 2SO_4 mass content 90%), stir and reacting by heating still to 80 DEG C, then in reactor, add 149Kg Klorvess Liquid (KCl mass content 50%), keep reactor temperature to be 80 DEG C of Keep agitation 30min, hydrogen chloride gas is all overflowed, obtains sal enixum slip 221.4Kg(KHSO_4 mass content 61.4%).

[0034] (2) magnesium oxide slip is prepared:

[0035] In plastic tank, add 40Kg magnesium oxide and 20Kg clear water, stir preparation and obtain magnesium oxide slip 60Kg (MgO mass content 66.7%) for subsequent use.

[0036] (3) neutralization reaction:

[0037] The magnesium oxide slip of (2) being joined joins in the sal enixum slip of (1) gained, reacting by heating still temperature to 120 DEG C, and Keep agitation reaction 5 ~ 10min obtains potassium magnesium sulfate slip.

[0038] (4) crushing drying is cooled:

[0039] Opening reactor discharge valve is put in stock pan by molten for the potassium magnesium sulfate of generation slurry, and be crushed to below 1mm after naturally cooling solidifies, oven drying at low temperature obtains potassium magnesium sulfate fertilizer product.

[0040] Embodiment 2:

[0041] (1) sal enixum slip is prepared:

[0042] The 105.4Kg vitriol oil (H is added in reactor 2SO_4 mass content 93%), stir and reacting by heating still to 120 DEG C, then in reactor, add 120.2Kg Klorvess Liquid (KCl mass content 62%), keep reactor temperature to be 120 DEG C of Keep agitation 45min, hydrogen chloride gas is all overflowed, obtains sal enixum slip 189.1Kg(KHSO_4 mass content 71.9%).

[0043] (2) magnesium oxide slip is prepared:

[0044] In plastic tank, add 40Kg magnesium oxide and 40Kg clear water, stir preparation and obtain magnesium oxide slip 80Kg (MgO mass content 50%) for subsequent use.

[0045] (3) neutralization reaction:

[0046] The magnesium oxide slip of (2) being joined joins in the sal enixum slip of (1) gained, reacting by heating still temperature to 140 DEG C, and Keep agitation reaction 5 ~ 10min obtains potassium magnesium sulfate slip.

[0047] (4) crushing drying is cooled:

- [0048] Opening reactor discharge valve is put in stock pan by molten for the potassium magnesium sulfate of generation slurry, and be crushed to below 1mm after naturally cooling solidifies, oven drying at low temperature obtains potassium magnesium sulfate fertilizer product.
- [0049] Embodiment 3:
- [0050] (1) sal enixum slip is prepared:
- [0051] The 123.8Kg vitriol oil (H is added in reactor 2SO_4 mass content 95%), stir and reacting by heating still to 140 DEG C, then in reactor, add 106.4Kg Klorvess Liquid (KCl mass content 70%), keep reactor temperature to be 140 DEG C of Keep agitation 60min, hydrogen chloride gas is all overflowed, obtains sal enixum slip 193.7Kg(KHSO_4 mass content 70.2%).
- [0052] (2) magnesium oxide slip is prepared:
- [0053] In plastic tank, add 40Kg magnesium oxide and 80Kg clear water, stir preparation and obtain magnesium oxide slip 120Kg (MgO mass content 33.2%) for subsequent use.
- [0054] (3) neutralization reaction:
- [0055] The magnesium oxide slip of (2) being joined joins in the sal enixum slip of (1) gained, reacting by heating still temperature to 160 DEG C, and Keep agitation reaction 5 ~ 10min obtains potassium magnesium sulfate slip.
- [0056] (4) crushing drying is cooled:
- [0057] Opening reactor discharge valve is put in stock pan by molten for the potassium magnesium sulfate of generation slurry, and be crushed to below 1mm after naturally cooling solidifies, oven drying at low temperature obtains potassium magnesium sulfate fertilizer product.
- [0058] The potash magnesium sulphate fertilizer inspection method specified in GB/T20937-2007 detects, and the index of the potash magnesium sulphate fertilizer that embodiment 1-3 obtains is as shown in the table:
- [0059] [image]

[0060] As can be known from the above table, the potassium magnesium sulfate product prepared through the inventive method all reaches potash magnesium sulphate fertilizer national standard (GB/T20937-2007) acceptable end product standard.

1. the production method of a potash magnesium sulphate fertilizer, it is characterized in that: it with Repone K, the vitriol oil and magnesium oxide for raw material, Repone K and strong sulfuric acid response obtain sal enixum slip, sal enixum slip obtains potassium magnesium sulfate slip with magnesium oxide slip again, and namely potassium magnesium sulfate slip obtains potash magnesium sulphate fertilizer through cooling, fragmentation, baking operation.

2. the production method of a kind of potash magnesium sulphate fertilizer according to claim 1, is characterized in that: the preparation method of described potassium magnesium sulfate slip comprises the following steps:

Prepare sal enixum slip: potassium chloride and vitriol oil mix and blend react 30-60min, hydrogen chloride gas is overflowed to obtain sal enixum slip, and wherein control temperature of reaction 80 ~ 140 DEG C, the mol ratio of Repone K and the vitriol oil is with KCl and H_2SO_4 count 1:1 ~ 1.2;

(2) magnesium oxide slip is prepared: according to quality than magnesium oxide: water=1:0.5 ~ 2, magnesium oxide is mixed obtained magnesium oxide slip with water;

(3) potassium magnesium sulfate slip is prepared: the sal enixum slip obtained by step (1) and the magnesium oxide slip Hybrid Heating of step (2) are reacted 5 ~ 10min and namely obtained potassium magnesium sulfate slip, wherein controlling temperature of reaction is 120 ~ 160 DEG C, and the mol ratio of sal enixum slip and magnesium oxide slip is with $KHSO_4$ 1:1 is got with MgO meter.

3. the production method of a kind of potash magnesium sulphate fertilizer according to claim 2, is characterized in that: described in step (1), Repone K mixes with the vitriol oil in the form of a solution, wherein concentration $\geq 50\%$ of Klorvess Liquid.

4. the production method of a kind of potash magnesium sulphate fertilizer according to claim 2, is characterized in that: concentration $\geq 90\%$ of the vitriol oil described in step (1).

5. the production method of a kind of potash magnesium sulphate fertilizer according to claim 2, is characterized in that: the hydrogen chloride gas grading absorption that described step (1) is overflowed makes hydrochloric acid.

AB	- NOVELTY : Potassium magnesium fertilizer preparation involves taking potassium chloride, concentrated sulfuric acid and magnesium oxide as raw material, and then reacting potassium chloride and concentrated sulfuric acid to obtain potassium hydrogen sulfate slurry. The obtained material is reacted with magnesium oxide material to obtain potassium magnesium sulfate material, and then the obtained material is cooled. The obtained material is crushed, and then dried to obtain the finished product. - ACTIVITY : Fertilizer. - USE : Method for preparing potassium magnesium fertilizer (claimed). - ADVANTAGE : The method enables to prepare potassium magnesium fertilizer in a cost-effective manner, ensures improved yield. - PHARMACEUTICALS : Preferred Conditions: Potassium hydrogen sulfate slurry is obtained at 80-140 [deg] C, where molar ratio of potassium chloride and concentrated sulfuric acid is 1:1-1.2. Magnesium oxide material is prepared by mixing magnesium oxide and water in 1:0.5-2 ratio. Potassium hydrogen sulfate slurry and magnesium oxide material are mixed in 1:1 ratio for 5-10 minutes at 120-160[deg] C.
AN	- 2015-18845V
AP	- ~~CN20141526143~~ 20141009
CN	- R10172-K R10172-P R01678-K R01678-S R01714-K R01714-S R07673-K R07673-S R01510-K R01510-S
CPY	- LOMO-N
DC	- C04
DCR	- [1] 131185 CL PRD; 127 CL RCT; 7 CL RCT; 157 CL RCT
DR	- 1678-S 1714-S 1510-S
DW	- 201525
ICAI	- C05D1/02
IN	- LI B; YANG L; ZHANG H
INW	- LI B; YANG L; ZHANG H
IW	- PREPARATION POTASSIUM MAGNESIUM FERTILISER CHLORIDE CONCENTRATE SULPHURIC ACID OXIDE RAW MATERIAL REACT OBTAIN HYDROGEN SULPHATE SLURRY
IWW	- PREPARATION POTASSIUM MAGNESIUM FERTILISER CHLORIDE CONCENTRATE SULPHURIC ACID OXIDE RAW MATERIAL REACT OBTAIN HYDROGEN SULPHATE SLURRY
M2	- [01] A119 A212 A940 C108 C316 C540 C730 C801 C802 C803 C804 C805 M411 M720 M904 M905 N200 N513 P111 P112; R10172-K R10172-P - [02] A119 A940 C017 C100 C730 C801 C803 C804 C805 C806 C807 M411 M730 M904 M905 M910; R01678-K R01678-S - [03] C101 C108 C316 C540 C730 C800 C801 C802 C804 C805 M411 M730 M904 M905 M910; R01714-K R01714-S R07673-K R07673-S - [04] A212 A940 C108 C550 C730 C801 C802 C803 C804 C805 C807 M411 M730 M904 M905 M910; R01510-K R01510-S
MC	- C05-A01 C05-C05 C14-T03 C14-T05

NC	- 1
NPN	- 1
OPD	- 2014-10-09
PA	- (LOMO-N) LOMON LAND AGRIC CO LTD
PAW	- (LOMO-N) LOMON LAND AGRIC CO LTD
PD	- 2015-01-28
PN	- CN104311164 A 20150128 DW201525
PR	- CN20141526143 20141009
TI	- Preparing potassium magnesium fertilizer, involves taking potassium chloride, concentrated sulfuric acid and magnesium oxide as raw material, and then reacting potassium chloride and sulfuric acid to obtain potassium hydrogen sulfate slurry
UPA	- 20150417
UPM	-

PATENT SPECIFICATION

NO DRAWINGS

Inventor: JOHN CONRAD ARNOLD (DECEASED)

828,883



Date of Application and filing Complete Specification Nov. 28, 1955.

No. 27936/59.

(Divided out of No. 828,881).

Complete Specification Published Feb. 24, 1960.

Index at acceptance:—Classes 1(3), A1(D37:G2D37); and 111, B3C(1:2:3:4:5), B3(D6:E).

International Classification:—C01b, C05b, c, d, f.

COMPLETE SPECIFICATION

Production of Fertilizers

I, CHARLES HENRY JOURDAN, of "Gracefield," Lacey Green, near Princes Risborough, Buckinghamshire, a British subject [the personal representative of John Conrad Arnold, deceased, late of 9, Staple Inn, London,

The term "fertilizer ingredient" as used in this specification, means any ingredient which is useful *per se* as a fertilizer as opposed to an ingredient requiring chemical conversion before becoming useful.

SPECIFICATION NO. 828,883

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of Facerform Company, a company duly registered under the laws of the State of New Jersey, United States of America, of 300 Pascack Road, Ridgewood, New Jersey, United States of America.

THE PATENT OFFICE,

22nd January, 1960

DB 29308/1(11)/3898 200 1/60 R

In accordance with the invention there is provided a process for the manufacture of a fertilizer product in which a solid fertilizer raw material is reacted with an inorganic acid material, characterised in that said solid fertilizer raw material is reacted with a preponderantly dry acidic sludge which contains the inorganic acid material together with a fertilizer ingredient, said fertilizer ingredient, fertilizer raw material and acid material being such as to result in a dry mixed fertiliser, the process being carried out in the absence of extraneously applied heat and without artificial drying of the product.

The term "fertilizer raw material" used in this specification means a material which contains a plant-nutritive element, not necessarily a primary plant-nutritive element, and which, as a result of the reaction with inorganic acid material, is rendered useful or more useful as a plant nutrient. Specific fertilizer raw materials are phosphate rock and dolomitic limestone, alone or in combination.

With excess sulphuric acid to form, respectively, an ammonium sulphate/sulphuric acid sludge and a potassium sulphate/sulphuric acid sludge. If necessary, additional acid may be added to the sludges so formed to bring the acid potential up to the level required to acidulate the whole of the fertilizer raw material.

It is an essential characteristic of the invention that the sludge does not contain sufficient moisture as to be a slurry which can be pumped, but is a preponderantly solid mass which is palpably moist. During an early stage of its formation it may pass through a liquid stage but it soon partakes chiefly of the characteristics of dry material, as does a mixture of phosphate rock and liquid acid. As illustrative only it may be said that this sludge may have three parts by weight in the dry phase and one part in the wet phase. Certain of these sludges resemble fine wet sand in which is often termed a "drip-dry" condition.

All that is required to carry out the acidulation of the raw material is for the sludge

[Price 3s. 6d.]

PATENT SPECIFICATION

NO DRAWINGS

Inventor: JOHN CONRAD ARNOLD (DECEASED)



828.883

Date of Application and filing Complete Specification Nov. 28, 1955.

No. 27936/59.

(Divided out of No. 828,881).

ERRATA

SPECIFICATION NO. 828,883

Page 1, line 17 and line 32, (in both occurrences)

Page 2, line 23, for "fertilisers" read "fertilizers"

Page 1, line 17, after "i.e." delete "comma"

Page 1, line 54, after "dient" insert "full stop"

Page 2, line 64, after "wherein" insert "comma"

Page 2, line 66, after "curing" insert "comma"

Page 2, line 78, for "obligation" read "application"

Page 3, line 27, after "thereafter" delete "comma"

Page 3, line 118, for "liquids" read "liquid"

Page 3, line 128, for "with" read "With"

Page 4, line 81, for "HCL" read "HCl"

Page 4, line 82, for "KCL" read "KCl"

Page 5, line 18, after "solid" insert "comma"

Page 5, line 62, for "fixed" read "fixed"

Page 5, line 119, for "materials" read "material"

Page 6, line 52, after "carbonate" insert "comma"

Page 7, line 46, after "lizer" insert "ingredient, said fertilizer"
"ingredient, fertilizer"

THE PATENT OFFICE,
19th July, 1961

DS 94615/1(11)/R.153 200 7/61 PL

40 a primary plant-nutritive element, and which, as a result of the reaction with inorganic acid material, is rendered useful or more useful as a plant nutrient. Specific fertilizer raw materials are phosphate rock and dolomitic limestone, alone or in combination.

[Price 3s. 6d.]

...necessarily
...may have three parts by weight in the dry phase and one part in the wet phase. Certain of these sludges resemble fine wet sand in which is often termed a "drip-dry" condition. All that is required to carry out the acidulation of the raw material is for the sludge

PATENT SPECIFICATION

NO DRAWINGS

Inventor: JOHN CONRAD ARNOLD (DECEASED)

828,883

Date of Application and filing Complete Specification Nov. 28, 1955.

No. 27936/59.

(Divided out of No. 828,881).

Complete Specification Published Feb. 24, 1960.



Index at acceptance:—Classes 1(3), A1(D37: G2D37); and 111, B3C(1:2:3:4:5), B3(D6:E).

International Classification:—C01b, C05b, c, d, f.

COMPLETE SPECIFICATION

Production of Fertilizers

I, CHARLES HENRY JOURDAN, of "Gracefield," Lacey Green, near Princes Risborough, Buckinghamshire, a British subject [the personal representative of John Conrad Arnold, deceased, late of 9, Staple Inn, London, W.C.1] do hereby declare the invention (a communication from FACERFORM COMPANY, a company duly registered under the laws of the State of New Jersey, United States of America, of 300, Pascack Road, Ridgewood, New Jersey, United States of America), for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for the preparation of mixed fertilisers, i.e., fertilisers which provide, in available form, two or more plant-nutritive elements, at least one of which is a primary plant-nutritive element, viz. phosphorus, potassium or nitrogen.

In accordance with the invention there is provided a process for the manufacture of a fertilizer product in which a solid fertilizer raw material is reacted with an inorganic acid material, characterised in that said solid fertilizer raw material is reacted with a preponderantly dry acidic sludge which contains the inorganic acid material together with a fertilizer ingredient, said fertilizer ingredient, fertilizer raw material and acid material being such as to result in a dry mixed fertiliser, the process being carried out in the absence of extraneously applied heat and without artificial drying of the product.

The term "fertilizer raw material" used in this specification means a material which contains a plant-nutritive element, not necessarily a primary plant-nutritive element, and which, as a result of the reaction with inorganic acid material, is rendered useful or more useful as a plant nutrient. Specific fertilizer raw materials are phosphate rock and dolomitic limestone, alone or in combination.

The term "fertilizer ingredient" as used in this specification, means any ingredient which is useful *per se* as a fertilizer as opposed to an ingredient requiring chemical conversion before becoming useful.

As acidic sludges there may be used any sludge or combination of sludges containing an inorganic acid material, such as sulphuric acid and/or phosphoric acid, and a fertilizer ingredient

The fertilizer ingredient may contain one or more of the following plant-nutritive elements, viz. nitrogen, phosphorus, potassium, calcium, magnesium or sulphur. In the simplest case the sludges may be prepared by mixing the fertilizer ingredient with the acid material, but preferably the sludge is formed by reacting a suitable precursor of the fertilizer ingredient with excess acid, for example, by reacting ammonia or potassium chloride with excess sulphuric acid to form, respectively, an ammonium sulphate/sulphuric acid sludge and a potassium sulphate/sulphuric acid sludge. If necessary, additional acid may be added to the sludges so formed to bring the acid potential up to the level required to acidulate the whole of the fertilizer raw material.

It is an essential characteristic of the invention that the sludge does not contain sufficient moisture as to be a slurry which can be pumped, but is a preponderantly solid mass which is palpably moist. During an early stage of its formation it may pass through a liquid stage but it soon partakes chiefly of the characteristics of dry material, as does a mixture of phosphate rock and liquid acid. As illustrative only it may be said that this sludge may have three parts by weight in the dry phase and one part in the wet phase. Certain of these sludges resemble fine wet sand in which is often termed a "drip-dry" condition.

All that is required to carry out the acidulation of the raw material is for the sludge

and the ground raw material to be mixed in a manner generally known in fertilizer technology as "dry-mixing". After the physical mixing is completed the acid is allowed to permeate the mass for a short while, but it is generally not necessary to place the mixture in a den, whether of the stationary type or the continuous type, to set as is the case in many fertilizer processes particularly those using slurries. No extraneous heat is applied at any stage in the process nor is any artificial drying of the product required, and, furthermore, it is not necessary either to employ any neutralization step or any extensive curing period, one short cure, if any, is all that is needed.

The process of the invention may thus be carried out in relatively simple and inexpensive apparatus and without the highly skilled technical management which is required in the great majority of conventional processes for making mixed fertilisers. Furthermore, the process is carried out in a greatly reduced time since there is no requirement for any drying operations, the sludge providing substantially all the moisture required at any time for securing the needed chemical reactions but not to excess, and with lower handling costs since the circulating load is substantially that of the finished product.

At any time during the mixing of the sludge or the subsequent dry-mixing of the sludge and raw material, additional fertilizer ingredients in dry form such as potassic or nitrogenous material, or metallic salts useful for plant-growth, may be added to produce a three or more component mixed fertilizer. Such metallic salts may, of course, already be present in the fertilizer raw material.

At the end of the mixing operation and after the acid has been allowed to permeate the mass, the mixed fertilizer product may be broken up, pelleted if desired, and stored or otherwise handled ready for use.

When processing phosphate rock, which may be any raw phosphate or phosphatic ore, it is preferred that the process be performed and the product cured according to the process claimed in copending Application No. 30469/55 (Serial No. 828,881), from which this present application has been divided and according to which a fertilizer containing phosphate is manufactured by a process which comprises mixing an inorganic acid material and phosphate rock, the resulting product tending to set and develop heat, and after the digestive mass has hardened to such an extent as to be disintegrable without coalescing, breaking up the digestive mass, subsequent further hardening as well as curing of the broken-up mass taking place, thereafter curing said mass at normal pressure, and obtaining a sensibly dry free-flowing cured fertilizer product, wherein from the time the mass is so broken up to the practical comple-

tion of curing (a) substantially no evaporation of the water content of the mass undergoing curing takes place and cooling goes on substantially continuously, and (b) the water content of the mass undergoing curing is such that the sensibly dry free-flowing cured fertilizer product which results from the process has been dried substantially entirely by crystallization alone.

In a practical method of performing the present invention in accordance with the teachings of said copending application, hereinafter called the parent obligation, and to achieve the full agronomic benefits as set forth in the specification thereof, the reaction mixture, when it has hardened sufficiently to be disintegrable without coalescing, is broken up and heaped in piles, which piles are provided with ventilating passages extending thereinto such that the exothermic heat developed by the broken up mass during curing is transmitted substantially directly to the atmosphere the temperature of the broken-up mass decreasing substantially continuously to the practical completion of curing. For further details of such method, reference is directed to the specification of said parent application.

More preferably still, the product from the reaction of the acidic sludge and a phosphate rock is disintegrated into discrete particles and pelleted by the process claimed in a second copending application, No. 27464/59 (Serial No. 828,882), also a divisional from the parent application and according to which a pelleted fertilizer is manufactured by a process which comprises providing small discrete particles of the product of the primary reaction between an inorganic acid material and phosphate rock, the surfaces of which particles are moist and acidic, moving the discrete particles upon themselves while they are still moist and acidic from the primary reaction to form agglomerates approaching the size of the pellets desired and, while continuing said movement, coating the agglomerates with an absorptive, finely divided material which forms a permanent thin layer thereon to physically complete the pellets, wherein, throughout the agglomeration and coating operations (a) all internal chemical reactions resulting from the acidity of the material are permitted to proceed unhindered by extraneous heating or neutralization, and (b) the water content of the material being agglomerated and coated is such as to permit the interiors of the pellets to dry substantially entirely by crystallization alone, the foregoing steps alone serving to result in a firm, physically completed, sensibly dry free-flowing pellets.

As the finely-divided coating material there may be used any material which under the conditions forms a continuous closed enveloping shell of appreciable thickness sufficient to physically support the pellets but it is preferred that the coating material is reactive with

the surface acid of the agglomerates and is either itself a fertilizer ingredient, or is capable of yielding a fertilizer ingredient upon acidulation. Suitable finely-divided materials which may be mentioned are ground phosphate rock, ground dolomite, charcoal, bone black, bone char, lamp black, nitrogen-bearing organic materials including animal tankage and cottonseed meal, and potassic or phosphatic dusts.

For further details of forming such a pelleted fertilizer reference is directed to the specification of said second copending application.

Perhaps the most useful fertilizer ingredients used in the acidic sludges of the present invention are nitrogen (ammonia), phosphorus and potassium, as well as sulphur and calcium.

A nitrogen-bearing inorganic acidic sludge particularly useful for the practice of this invention is obtained as a by-product of the destructive distillation of coal. In known processes of making ammonium sulphate, after the ammonia in sulphuric acid used for purification of gas or other similar purposes has been trapped, the resulting slurry is ordinarily centrifuged and then neutralized with material having no fertilizer value. Thereafter, it is sold as finished ammonium sulphate which is the most widely used source of nitrogen throughout the world in mixed fertilizers made from finished ingredients. These known practices mix ammonium sulphate and superphosphate, each a completely finished dry product, to form a mixed fertilizer containing nitrogen and phosphate. This mixture often must also be neutralized and cured for a short period. According hereto a combined product containing both fertilizer ingredients is made in a single operation with no neutralization by any material which is of no use to plant growth.

According to the processes herein sulphuric acid in a by-product operation is utilized in a purification operation to trap ammonia until approximately 75% of the acidic ammonium sulphate is in solid form and the acidic potential of the entire mass is at least 52° B. This operation preferably is carried beyond the usual point past the point of saturation and by the employment of an acid which is of higher concentration than usually employed more ammonia is trapped and a more solid sludge formed. Contrary to conventional practice 15% or more nitrogen can be trapped because the operation carries the absorption beyond the point at which the sulphate of ammonia in the sulphuric acid acts as a diluent. Use of sulphuric acid in this unusually high degree of concentration for such a purpose is economically possible because it quickly traps the maximum amount of ammonia and by the following steps all of the acid potential is properly employed. Alternatively any ammoniacal solution may be fed through relatively concentrated sulphuric acid beyond the point of

saturation as above. Phosphoric acid may be used in place of sulphuric thereby increasing the phosphatic component of the mixed fertilizer. After the ammonia is trapped and the high heat of the primary reaction has passed the quantity of fertilizer raw material necessary to utilize the acidic potential is mixed with the mass. If the product is to be fine all of the phosphate rock may be mixed with the sludge at one time. If the product is to be pelleted, as is preferred, the phosphate rock is added in two increments, one to bring the original mixture to the point at which it will agglomerate readily, and the other to coat the agglomerations when made. Ammonium sludge so produced may be mixed with other acidic sludges, as later described herein. If a potassic sludge is added, a complete fertilizer results. Such practices produce finished mixed fertilizers at a reduced cost in labor and capital and in shorter time.

For many purposes, particularly when the manufacture of mixed fertilizers is carried out in small manufacturing establishments without extensive equipment commercial ammonium sulphate may be mixed with sulphuric and/or phosphoric acid to form an acidic sludge of the above characteristics and thereupon the fertilizer raw material may be added. Since the addition of the raw material to the preponderantly dry sludge is mechanically simple and the mass does not set hard it can be formed into agglomerations and coated with equipment designed for substantially dry products and much more simple than that of a conventional superphosphate plant. One may advantageously mix sulphuric acid with commercial ammonium sulphate and handle the resulting mixture as hereinabove described.

EXAMPLE 1

Absorb 269 pounds of ammonia in 1423 pounds of sulphuric acid calculated at 60° B. and 60° F. and preferably used at that concentration. Mix intimately with 530 pounds of phosphate rock. The acidic potential of the mixture as the rock is introduced should be at least 52° B. and the high heat of the ammonia absorption should have subsided. The absorption operation is carried beyond the point of saturation at which solid ammonium sulphate appears and is continued until the ratio is substantially 3 parts of solid ammonium sulphate or more to 1 part by weight of free liquids. After the completion of the primary chemical reaction, form the mixture into discrete particles and by movement upon themselves forms agglomerations and coat them with 120 pounds of additional rock and preferably cure the pellets in accordance with the teachings of said parent application. Alternatively, if fine superphosphate is wanted, use a total of 650 pounds of rock in the original mixture, with ordinary Florida rock of 72% bone phosphate of lime the resulting product analyses 11.25—9.43—0. A total of 650 pounds of rock

70

75

80

85

90

95

100

105

110

115

120

125

130

is used instead of the theoretical total of 623 pounds because of the greater acidulating potential of the sulphate.

- 5 Other fertilizer ingredients in dry form may be added to the ammonia sulphate sludge as, for example, potassium, in order to make a complete three-element product, as is illustrated as follows:—

EXAMPLE 2

- 10 Prepare 2625 pounds of sludge as in Example 1. Add 1112 pounds of ground phosphate rock and 667 pounds of dry potassium chloride. Mix. At the completion of the primary reaction disintegrate, then agglomerate and add 200 pounds of ground phosphate rock as coating when the agglomerations approach the desired size. The result is a complete mixed fertilizer of an approximate analysis of 8.2—9.5—8.7. If a fine fertilizer
- 15 is desired the sludge and the dry materials may be more slowly mixed, without subsequent agglomeration. No appreciable amount of hydrogen chloride will be released because the sulphuric acid is not in excess.

- 20 Another sludge which may be used in the process of the invention is a low-chlorine potassium sludge, formed by reaction of potassium chloride with sulphuric acid. Such a sludge serves as the basis of a potassium-phosphate mixed fertilizer which may contain as little as 2% of chlorine. Chlorine in sub-

stantial quantities or for often repeated heavy applications is considered injurious to many plants, but a product with as little chlorine as 2% is accepted without question. Potassium chloride is the form in which a large proportion of all potassium in use for fertilizer material is mined and sold. Known processes convert potassium chloride to potassium sulphate by mixing for many hours with sulphuric acid under high heat. Such costly products have been referred to and are officially designated in many countries as potassium sulphate although containing 3% or more of chlorine in the total fertilizer.

To form a low-chlorine potassium sludge for use in the process of the invention, a large excess of concentrated sulphuric acid is added to the potassium chloride, and the mixture stirred for a few minutes and in the absence of externally applied heat to evolve chlorine as hydrogen chloride and to produce an acidic potassium sludge. After the chlorine is evolved and removed, this acidic sludge is used to acidulate ground phosphate rock. The excess of concentrated sulphuric acid acting on the potassium chloride drives off any desired amount of the chlorine up to about 94%. It is preferred to use 52 to 60° B. sulphuric acid. The following table illustrates the removal of chlorine:—

	H ₂ SO ₄ 60° B.	KCl	Cl Removed	%	Acid Consumed	Acid Unused	Rock Used	P ₂ O ₅ %	K ₂ O %
65	100	10	4.4	93	7.92	92.1	138	18.9	2.5
	100	30	11.35	80	20.43	79.57	119	16.7	7.7
	100	60	21.28	75	38.34	61.66	92.5	13.7	16.1

All values except as noted are in pounds.

- 70 After having chosen the proportions of sulphuric acid and potassium chloride according to the relations indicated above, the acid and potassium chloride are mixed and stirred for a few minutes. If a fertilizer raw material other than phosphate rock, which has an "acid-rock" factor of 2.3, is used, other values must be changed accordingly. The evolved hydrogen chloride gas is passed through a water bath to form hydrochloric acid, which is sold as a by-product.

- 75 The sludge produced contains KHSO₄ and H₂SO₄ with some K₂SO₄ and a slight amount of HCL which has not been completely removed as well as the KCL from which the chlorine has not been evolved. An amount of fertilizer raw material sufficient to utilize the total acidic potential is then mixed with the acid potassium sludge. After the primary chemical reaction is complete, the mass preferably is made into agglomerations and coated as in Example 1 although it may be stored as fine material, preferably in a ventilated pile as described in the parent application. No external heat is applied at any time.

EXAMPLE 3

A product with the formula 0—14—15 containing about 2½% of chlorine may cheaply, quickly and easily be produced by the above process. To form the acidic sludge stir 880 pounds of potassium chloride with 1512 pounds of sulphuric acid (60° B. at 60° F.) for about 5 minutes. After about 300 pounds of hydrogen chloride gas has been evolved and removed, mix with 1325 pounds of phosphate rock. The evolved chlorine represents 75% of the total originally present. After the primary reaction is substantially complete form the mixture into discrete particles and promptly move them upon themselves until agglomerations with acid-wetted surfaces approaching the desired size are built up and coat them with 175 pounds additional of phosphate rock. Alternatively, the sludge may be mixed with 1440 pounds of phosphate rock and the product cured in said ventilated-pile, to give a fine cured product.

Alternatively potassium sulphate, finished or crude, may be mixed with the acid of usual concentration to form an acidic sludge which can be mixed with the fertilizer raw material,

with or without the addition of other sludges.

Another aspect of the processes herein is the employment of dolomite to furnish water-soluble magnesium, a product recommended by many agronomists for many types of soils preferably in combination with phosphates. In the above examples dolomite may well be substituted for at least a portion of the phosphate rock and/or as a coating for the pelleted product.

In connection with magnesium one must consider the question of water-solubility in its true meaning in connection with fertilizer base materials and ingredients.

Water-solubility refers to the dissolution of a substance in water to form a solution in which the concentration of each element in the solution is the same as that in the solid, i.e. the dissolution is reversible. Water-extractability refers to the disappearance of certain or all the parts of a substance whether the liquid extract is a true solution of the original solid or not.

In conventional processes when ammonium hydroxide has been added to monocalcium phosphate in the presence of calcium sulphate the resulting products have been dicalcium phosphate and ammonium sulphate. Thus no water-soluble or water-extractable phosphatic product has resulted. When alkali metals, however have been combined with phosphorus to form acidic salts, truly water-soluble phosphates of these metals have been formed. Unlike conventional monocalcium phosphate, monomagnesium phosphate is soluble in water and hence has formed no problem when used alone or in combination only with phosphorus, as has been done successfully in the past. In ordinary superphosphate, however, soluble magnesium phosphate appears only in negligible quantities while water-extractable monocalcium phosphate is present in relatively large volume. Dolomitic limestone has been added to cured superphosphate to react with the free acid of the fertilizer and render additional quantities of magnesium water-soluble. If certain metals are present in sulphate form, this added dolomite will render them insoluble. If such metals are temporarily in an acid environment owing to the free acid and hence acid-soluble for the moment, they will be made insoluble by this neutralizing process. This process, however, makes it possible to produce a fertilizer in which magnesium, phosphorus, iron and other metals exist together in water-soluble and available forms. The value of such metals or "trace elements" in many soils is now widely recognized.

Dolomitic limestone is applied to certain soils to furnish, as it is slowly digested in the soil, magnesium and calcium hydroxide which change the pH balance of the soil and by substitution or replacement make otherwise fixed potassium therein assimilable by plants. This slow process is comparable to the direct application of phosphate rock to the soil. Magnesium

salts applied as such to the soil hasten, often by years, the agronomic advantages secured from dolomitic limestone, but when prepared and used alone it is expensive. According to this process dolomitic limestone (like phosphate rock) is acidulated so that its benefits in full measure become almost immediately available. Moreover, the product hereof includes water-soluble magnesium phosphate. Magnesium in combination with phosphate, both in plant assimilable form, increase the value of each.

This phase is illustrated by a description of the production of a magnesium-potash base having 7% MgO and 25% K₂O of the latter of which approximately one-third is in the sulphate form and two-thirds in the chloride form. Ground dolomitic limestone and the above-described potash sludge of Example 3 are the base of this product. Dolomite contains up to 45% MgCO₃ and 55% of CaCO₃. An example follows:—

EXAMPLE 4

To form the acidic sludge, mix 1750 pounds of potassium chloride and an equal amount of sulphuric acid, 60° B. at 60° F., from 3 to 5 minutes. Where a dolomitic carbonate or hydroxide is used in place of ground phosphate rock, the amount is determined as that able to employ the acidic capacity of the sludge. The particular dolomite used in the above illustration has an "acid dolomite" factor of 1.15 which corresponds to an "acid rock" factor of 2.3 for the phosphate rock in the previous examples. In this case use 1650 pounds of ground dolomite.

If sufficient acidic potential is present, both the MgCO₃ and CaCO₃ are completely converted immediately, thereby forming a mixture of potassium, magnesium and calcium sulphate with no carbonates, but in the presence of insufficient acid for the complete conversion of both as above, the magnesium carbonate tends to decompose more rapidly than the calcium carbonate. Thus with insufficient acid for complete conversion more MgSO₄ is formed than CaSO₄. By mixing the above produced sludge and 1650 pounds of dolomite a net finished product after shrinkage of approximately 3200 pounds is secured. This product is granular, dry and free-flowing and can be shipped within a few hours after mixing although the solubility of the magnesium will slowly increase. If 300 pounds of the above raw materials are used in a short ton of fertilizer the product contains 1% of magnesium oxide and 3½% of potash. The addition of 600 pounds of the above raw material to 1400 pounds of materials containing nitrogen and phosphorus furnishes 2% of MgO together with slightly more than 7% of potash in a short ton of a complete fertilizer.

The acid may be mixed with the potassium chloride in a pan mixer. After the desired

amount of HCl has been removed the dolomite is added. This entire mixing operation is carried on for several minutes. The mixture of dolomite and acidic potassium sludge sets quickly but not in a hard mass. The greater the amount of potassium the more granular and free-flowing the mixture and hence the more readily it can be mixed. Other variants include the amount of acid relative to the solids to evolve the chlorine. After mixing, the mass is merely put through a sizing device and is ready for use, although solubility of the magnesium will continue to increase.

It has been discovered, furthermore, that this operation whether on a batch or continuous basis may be advantageously carried out by division of the ground limestone on the basis of particle size. Since dolomitic limestone varies from hard to soft, the fineness with which the material is ground adds greatly to the cost. It previously has been considered necessary to grind dolomitic limestone finely. By this process, however, good results are secured by relatively coarse grinding, for example so that 40% will not pass through a 100 mesh screen and 60% will pass through. First this coarse portion and all of the acid necessary to complete the acidulation are mixed. There must be sufficient liquid acid to reach all these coarse particles. After a few minutes of mixing so that the acid has had opportunity to reach the entire mass and begin the digestive process the finer particles are added.

EXAMPLE 5

In the following example of this phase of this invention 2650 pounds of potassium chloride are mixed with an equal amount of sulphuric acid of 60° B. Then add 2405 pounds of dolomite, 955 pounds in the first instance and the balance of 1445 pounds later, namely, a ratio of about 2 to 3.

Particularly since a relatively small amount of water-soluble magnesium is required for many complete fertilizers, one may employ dolomite in part and ground phosphate rock in part to make effective use of the acidulating potential of the sludge.

In processing such a mixed raw fertilizer material one may use the previously described ammonium sulphate sludge to produce a magnesium-nitrogen-phosphate product. The ammonium carbonate which may be formed by the double decomposition of the ammonium sulphate and magnesium of calcium carbonate, tends to decompose into NH_3 , CO_2 and H_2O , but this process is either retarded or stopped if monocalcium phosphate is present. The following illustration will make this clear:—

EXAMPLE 6

2000 pounds of ammonium sulphate sludge are mixed with 400 pounds of dolomite and 500 pounds of phosphate rock to yield a finished net product of approximately 2850

pounds which analyzes 10.1% N, 2.95% MgO and 5.75% P_2O_5 .

The above principles may also be applied to the making of a complete fertilizer including the potassium low-chlorine base with phosphate rock, acid and dolomite.

The following fertilizer will have a formula of 6—8—10 with 2% of MgO:—

EXAMPLE 7

In a pan mixer, stir 618 pounds of sulphuric acid of 60° B. and 335 pounds of potassium chloride for 3 to 5 minutes, thereby driving off 85 pounds of HCl. The resulting sludge has a net weight of 868 pounds. To this sludge, add 500 pounds of phosphate rock and 100 pounds of dolomite and, after rock, acid and dolomite have made thorough contact, 585 pounds of conventional dry sulphate of ammonia. Pour the mass into a den and remove it therefrom after it has set, disintegrate it and pass it into a pelleting drum. In a late stage of the pelleting operation coat with an additional 100 pounds of ground dolomite.

A further acidic sludge which may be used results from the acidulation of ground phosphate rock with sulphuric acid which has the advantage that dilute phosphoric acid may be separated from the resultant gypsum sludge as a by-product. This gypsum sludge which still contains free acid may be combined just as it comes from the phosphoric acid process either with other sludges or used independently to acidulate fertilizer raw materials as hereinbefore set forth.

This gypsum sludge is valuable since it carries sulphur and calcium, which are needed for many soils. In the frequent instances in which fertilizers with these elements as well as nitrogen, phosphorus and potash of moderate concentration of a lower grade are needed, fertilizer raw materials are mixed with this gypsum phosphorus-bearing sludge while still moist, permitted to stand for a few minutes and disintegrated. Then the mass is moved upon itself to form agglomerations and coated as previously described. Almost all of the available phosphorus contained in the gypsum is thereby utilized.

This gypsum sludge makes possible a dry and pelleted product by the use of certain fertilizer ingredients which otherwise could not be handled readily. In the example which follows the phosphate rock performs the dual function of providing the fertilizer raw material to be digested and providing the finely divided coating material for the pellets.

EXAMPLE 8

A product of an analysis of 10—2—14 is made from 975 pounds of ordinary commercial sulphate of ammonia, 500 pounds of ordinary potassium chloride, 550 pounds of gypsum sludge of 3.2% P_2O_5 , and 75 pounds of ground phosphate rock, this amount of

coating material being slightly less than the usual 5% because of the slightly lowered moisture and free acid content of the mass. The ingredients other than the phosphate rock are mixed in an ordinary mixing pan and passed to a pelleting drum or its equivalent wherein it is moved upon itself and in a late stage of the agglomeration operation the phosphate rock is added as a coating. The result is a dry, free-flowing homogeneous pellet composed largely of nitrogen and potash but having enough phosphorus for many fertilizer purposes.

EXAMPLE 9

Such a phosphorus-bearing gypsum sludge is used for making a fertilizer useful for certain soils where gypsum is highly desirable but little phosphorus is needed. A complete fertilizer answering this need of an analysis of 6—5—6 is made by mixing 900 pounds of gypsum sludge having 3.2% of P_2O_5 , 200 pounds of potassium chloride, 675 pounds of sulphate of ammonia sludge prepared as above and containing 17.8% of nitrogen, and 125 pounds of ground phosphate rock of 72% bone phosphate of lime. After preliminary mixing these materials are passed through a pelleting drum or otherwise agitated to form agglomerations, which are then coated with an additional 100 pounds of phosphate rock, thereby using a total of 225 pounds.

Alternatively, particularly when a low-grade fertilizer is wanted together with calcium and/or sulphur, commercial gypsum or a gypsum sludge without an acidic potential may be used in combination with another acidic sludge.

WHAT I CLAIM IS:—

1. A process for the manufacture of a fertilizer product in which a solid fertilizer raw material is reacted with an inorganic acid

material, characterised in that said solid fertilizer raw material is reacted with a preponderantly dry acidic sludge which contains the inorganic acid material together with a fertilizer raw material and acid material being such as to result in a dry mixed fertilizer, the process being carried out in the absence of extraneously applied heat and without artificial drying of the product.

2. A process according to Claim 1, wherein the inorganic acid material is sulphuric acid or phosphoric acid or a mixture of the two.

3. A process according to Claim 1 or 2, wherein said solid fertilizer raw material is ground phosphate rock or other phosphatic ore and/or ground dolomitic limestone.

4. A process according to any one of the preceding claims, and including the step of preforming the acidic sludge by reacting a precursor of the fertilizer ingredient with an excess of the inorganic acid material.

5. A process according to Claim 4, wherein said sludge is formed by absorbing ammonia in relatively concentrated sulphuric acid and carrying said absorption past the point at which solid ammonium sulphate separates.

6. A process according to Claim 4, wherein said sludge is prepared by reacting potassium chloride and sulphuric acid.

7. A process according to Claim 4, wherein said sludge is preformed by digesting phosphate ore by sulphuric acid and removing a dilute solution of phosphoric acid as a by-product.

8. A mixed fertilizer when prepared by a process as claimed in any one of the preceding claims.

D. YOUNG & CO.,

9, Staple Inn,

London, W.C.1,

Agents for the Applicant.

CN109650947A 20190419

EPO

SUBJECT OF THE INVENTION

Method for producing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid

[0001] Technical field

[0002] The invention is specifically a method for producing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid, and belongs to the technical field of comprehensive utilization of hazardous wastes and chemical fertilizer production.

[0003] Background technique

[0004] The halogen production industry produces a large amount of industrial waste sulfuric acid in the production process. Because of its low concentration and containing certain chlorides, it is difficult for other industries to comprehensively use. The national hazardous waste list is classified as hazardous waste HW34.

[0005] The potassium hydrogen sulphate used in agricultural production is KHSO_4 , which is a K-containing S-containing fertilizer because it is completely water-soluble and slightly acidic after hydrolysis, and is especially suitable for alkaline soil application. Potassium hydrogen sulfate can be prepared by reacting sulfuric acid with potassium chloride. The existing production technology and patent use concentrated sulfuric acid and potassium chloride to react under low temperature conditions to form potassium hydrogen sulfate, and the hydrogen chloride absorbed by the reaction absorbs hydrochloric acid by-product. In order to ensure the effective progress of the reaction, sulfuric acid is added in excess. The obtained material is a potassium hydrogen sulfate slurry containing residual sulfuric acid, which is a strong acidic material and cannot be directly used as a potassium hydrogen sulfate fertilizer. Therefore, it is generally used as an intermediate process raw material and phosphoric acid. After mixing and dissolving, ammonia is added to neutralize to obtain a ternary sulfur-based compound fertilizer containing N, P, and K.

[0006] Summary of the invention

[0007] The invention provides a method for producing potassium hydrogen sulfate from industrial waste sulfuric acid, which can be used as an economic raw material for industrial waste sulfuric acid to prepare potassium hydrogen sulfate product, which can be used as raw material for fertilizer

production or directly used for agricultural production, and can be directly used. The fully water-soluble, slightly acidic potassium hydrogen sulfate fertilizer applied is especially suitable for alkaline soil application.

- [0008] In order to solve the above technical problems, the present invention discloses a method for producing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid, comprising the following steps:
- [0009] (1) Preparation of potassium hydrogen sulfate slurry; concentration of $\geq 70\%$ industrial waste sulfuric acid and potassium chloride in a stirred reaction tank, control temperature $110-140^{\circ}\text{C}$, KCl and H_2SO_4 molar ratio $1:1.1-1:1.2$; reaction generated Hydrochloric acid uses a multi-stage water absorption method to produce hydrochloric acid by-products;
- [0010] (2) Dilution; the potassium hydrogen sulfate slurry prepared in the step (1) is added to a portion of the hot water to be diluted, and the weight concentration of potassium hydrogen sulfate is controlled to be $50-60\%$ to prepare a diluted potassium hydrogen sulfate slurry;
- [0011] (3) Neutralization; the diluted potassium hydrogen sulfate slurry prepared in the step (2) is added with a small amount of magnesium oxide in a proportion corresponding to the excess sulfuric acid, and the reaction is controlled at a temperature of $60-80^{\circ}\text{C}$ to neutralize excess sulfuric acid in the potassium hydrogen sulfate slurry. Obtaining a slurry of potassium hydrogen sulfate containing magnesium sulfate;
- [0012] (4) Cooling crystallization; cooling the potassium sulfate potassium sulfate slurry obtained in the step (3) to $30-35^{\circ}\text{C}$, and precipitating potassium hydrogen sulfate crystals and crystallization of magnesium sulfate monohydrate or magnesium sulfate heptahydrate;
- [0013] (5) Separating; the crystal slurry containing the potassium hydrogen sulfate crystal obtained by the step (4) and crystallizing magnesium sulfate monohydrate or magnesium sulfate heptahydrate is separated by filtration through a centrifuge to obtain a crystal containing a small amount of magnesium sulfate monohydrate or magnesium sulfate heptahydrate. Body state potassium hydrogen sulfate fertilizer.
- [0014] Further, wherein the concentration of $\geq 70\%$ industrial waste sulfuric acid described in the step (1) is $\geq 70\%$ industrial waste sulfuric acid in the halogen industry or $\geq 70\%$ industrial waste without organic matter and harmful impurities in other basic chemical industries sulfuric acid.

- [0015] Further, in the step (4), the cooling crystallization is cooled by natural cooling or indirect heat exchange.
- [0016] Further, the hot water used in the step (2) is from the filtrate containing potassium hydrogen sulfate and magnesium sulfate separated in the step (5).
- [0017] The main reactions of the above steps are:
- [0018] $\text{KCl} + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HCl}$
- [0019] $\text{H}_2\text{SO}_4 + \text{MgO} = \text{MgSO}_4 + \text{H}_2\text{O}$
- [0020] The invention has the following beneficial technical effects:
- [0021] The industrial waste sulfuric acid, which is difficult to reuse in other industries, is used as raw material to produce potassium hydrogen sulfate fertilizer. The industrial waste sulfuric acid in the hazardous waste list can be disposed of in large quantities. The cost of the potassium hydrogen sulfate raw material produced in this way is basically zero, and the economic advantage is obvious; Magnesium neutralizes excessive sulfuric acid to eliminate strong acidity, and finally obtains K-containing, Mg-containing, S-containing, fully water-soluble crystalline potassium hydrogen sulfate fertilizer which can be directly used for agricultural production. Potassium hydrogen sulfate fertilizer obtained by the production method, typical component 1: K₂O: 23.50%, MgO: 4%, S: 19.4%; typical component 2: K₂O: 26.50%, MgO: 4.5%, S: 22%; typical group Sub-3: K₂O: 25.00%, MgO: 4.4%, S: 20.5%; there are also different nutrient combinations between typical components.
- [0022] Detailed ways
- [0023] The invention is further illustrated by the following specific examples.
- [0024] Embodiment 1:
- [0025] The invention relates to a method for producing potassium hydrogen sulfate by industrial waste sulfuric acid, which adopts low-concentration industrial waste sulfuric acid produced by the halogen industry or industrial waste sulfuric acid which is free from organic substances and harmful impurities generated by other basic chemical industries, and is reacted with potassium chloride at a low temperature. A potassium hydrogen sulfate slurry is obtained, and a predetermined amount of magnesium oxide is added to neutralize excess sulfuric acid to form a small amount of magnesium

sulfate. The mixed slurry is cooled, crystallized, and centrifuged to obtain a K-containing, Mg-containing, S-containing potassium hydrogen sulfate fertilizer.

[0026] Further, the method for producing potassium hydrogen sulfate by the above industrial waste acid comprises the following steps:

[0027] (1) A potassium hydrogen sulfate slurry was prepared. The industrial waste sulfuric acid and potassium chloride having a concentration of $\geq 70\%$ are reacted in a stirred reaction tank at a controlled temperature of 120°C , and the molar ratio of KCl to H_2SO_4 is 1:1.1. Hydrogen chloride produced by the reaction produces a by-product of hydrochloric acid by multistage water absorption.

[0028] (2) dilution. The potassium hydrogen sulfate slurry prepared in the step (1) is diluted with a part of hot water (the filtrate returned by centrifugation is continuously formed), and the weight concentration of potassium hydrogen sulfate is controlled to 55% to prepare a diluted potassium hydrogen sulfate slurry.

[0029] (3) neutralize. The diluted potassium hydrogen sulfate slurry prepared in the step (2) is added with a small amount of magnesium oxide in a proportion corresponding to the excess sulfuric acid to stir the reaction, and the temperature is controlled at 70°C to neutralize excess sulfuric acid in the potassium hydrogen sulfate slurry to obtain a magnesium sulfate salt. Potassium hydrogen sulfate slurry.

[0030] (4) Cool the crystals. The potassium hydrogen sulfate slurry obtained in the step (3) was cooled to 33°C , and potassium hydrogen sulfate crystals were precipitated and crystallized with magnesium sulfate monohydrate or magnesium sulfate heptahydrate.

[0031] (5) Separation. The crystal slurry containing the potassium hydrogen sulfate crystals and the magnesium sulfate monohydrate or magnesium sulfate heptahydrate obtained in the step (4) is separated by filtration through a centrifuge to obtain a crystalline sulfuric acid which finally contains a small amount of magnesium sulfate monohydrate or magnesium sulfate heptahydrate. Hydrogen potassium fertilizer. The filtrate obtained by filtration is dissolved with potassium hydrogen sulfate and magnesium sulfate, and returned to the step (2) for dilution.

[0032] The main reactions of the above steps are:

[0033] $\text{KCl} + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HCl}$

[0034] $\text{H}_2\text{SO}_4 + \text{MgO} = \text{MgSO}_4 + \text{H}_2\text{O}$

[0035] Typical component 1: K₂O: 23.50%, MgO: 4%, S: 19.4%; typical component 2: K₂O: 26.50%, MgO: 4.5%, S: 22%; typical component 3: K₂O: 25.00%, MgO: 4.4%, S: 20.5%; there are also different nutrient combinations between typical components.

1. The invention relates to a method for producing potassium hydrogen sulfate fertilizer by industrial waste sulfuric acid, which comprises the following steps:

(1) Preparation of potassium hydrogen sulfate slurry; concentration of $\geq 70\%$ industrial waste sulfuric acid and potassium chloride in a stirred reaction tank, control temperature 110-140 ° C, KCl and H₂SO₄ molar ratio 1:1.1-1: 1.2; reaction generated Hydrochloric acid uses a multi-stage water absorption method to produce hydrochloric acid by-products;

(2) Dilution; the potassium hydrogen sulfate slurry prepared in the step (1) is added to a portion of the hot water to be diluted, and the weight concentration of potassium hydrogen sulfate is controlled to be 50-60% to prepare a diluted potassium hydrogen sulfate slurry;

(3) Neutralization; the diluted potassium hydrogen sulfate slurry prepared in the step (2) is added with a small amount of magnesium oxide in a proportion corresponding to the excess sulfuric acid, and the reaction is controlled at a temperature of 60-80 ° C to neutralize excess sulfuric acid in the potassium hydrogen sulfate slurry. Obtaining a slurry of potassium hydrogen sulfate containing magnesium sulfate;

(4) Cooling crystallization; cooling the potassium sulfate potassium sulfate slurry obtained in the step (3) to 30-35 ° C, and precipitating potassium hydrogen sulfate crystals and crystallization of magnesium sulfate monohydrate or magnesium sulfate heptahydrate;

(5) Separating; the crystal slurry containing the potassium hydrogen sulfate crystal obtained by the step (4) and crystallizing magnesium sulfate monohydrate or magnesium sulfate heptahydrate is separated by filtration through a centrifuge to obtain a crystal which finally contains a small amount of magnesium sulfate monohydrate or magnesium sulfate heptahydrate. Body state potassium hydrogen sulfate fertilizer.

2. A method for producing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid according to claim 1, characterized in that the concentration of the industrial waste sulfuric acid in the

step (1) is $\geq 70\%$, and the industrial waste sulfuric acid of the halogen industry is $\geq 70\%$ or Other basic chemical industry $\geq 70\%$ industrial waste sulfuric acid free of organic matter and harmful impurities.

3.A method for producing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid according to claim 1, characterized in that, in the step (4), the cooling crystallization is cooled by natural cooling or indirect heat exchange.

4.A method of producing potassium hydrogen sulfate by industrial waste sulfuric acid according to claim 1, wherein the hot water used in the step (2) is obtained from the filtrate containing potassium hydrogen sulfate and magnesium sulfate separated in the step (5).

- AB**
- **NOVELTY** : Preparing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid comprises (i) reacting industrial waste sulfuric acid and potassium chloride in stirring reaction tank to obtain hydrogen chloride; (ii) adding obtained potassium hydrogen sulfate slurry into partial hot water dilution; (iii) adding small amount of magnesium oxide into diluted potassium hydrogen sulfate slurry, stirring to neutralize and remove excess sulfuric acid; (iv) cooling slurry of potassium hydrogen sulfate containing magnesium sulfate, precipitating crystals of potassium hydrogen sulfate and crystallizing with magnesium sulfate monohydrate or magnesium sulfate heptahydrate; and (v) separating crystal slurry containing potassium hydrogen sulfate crystal and magnesium sulfate monohydrate or magnesium sulfate heptahydrate by centrifuging and filtering.
 - **DETAILED DESCRIPTION** : Preparing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid comprises (i) reacting industrial waste $\geq 70\%$ sulfuric acid and potassium chloride in stirring reaction tank at $110-140^{\circ}\text{C}$ with molar ratio of potassium chloride and sulfuric acid of 1:1.1-1:1.2 to obtain hydrogen chloride, which uses multi-stage water absorption method to produce hydrochloric acid by-products; (ii) adding 50-60 wt.% obtained potassium hydrogen sulfate slurry into partial hot water dilution to obtain diluted potassium hydrogen sulfate slurry; (iii) adding small amount of magnesium oxide into diluted potassium hydrogen sulfate slurry in proportion corresponding to excess sulfuric acid, stirring the reaction at $60-80^{\circ}\text{C}$ to neutralize and remove excess sulfuric acid from potassium hydrogen sulfate slurry to obtain slurry of potassium hydrogen sulfate containing magnesium sulfate; (iv) cooling slurry of potassium hydrogen sulfate containing magnesium sulfate to $30-35^{\circ}\text{C}$, precipitating crystals of potassium hydrogen sulfate and crystallizing with magnesium sulfate monohydrate or magnesium sulfate heptahydrate; and (v) separating crystal slurry containing potassium hydrogen sulfate crystal and magnesium sulfate monohydrate or magnesium sulfate heptahydrate by centrifuging and filtering to obtain crystalline potassium hydrogen sulfate fertilizer containing small amount of magnesium sulfate monohydrate or magnesium sulfate heptahydrate.
 - **ACTIVITY** : Fertilizer.
 - **USE** : The method is useful for preparing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid.
 - **ADVANTAGE** : The method utilizes industrial waste sulfuric acid, which suitable for effect of alkaline soil application and can be directly applied to full water-soluble slightly acidic potassium hydrogen sulfate fertilizer.
 - **INORGANIC CHEMISTRY** : Preferred Components: The $\geq 70\%$ industrial waste sulfuric acid is $\geq 70\%$ industrial waste sulfuric acid in halogen industry or $\geq 70\%$ industrial waste sulfuric acid containing no organic matter and harmful impurities in other basic chemical industries. Preferred Method: In the step (iv), cooling crystallization is cooled by natural cooling or indirect heat exchange. The hot water used in the step (ii) is obtained from filtrate containing potassium hydrogen sulfate and magnesium sulfate separated in step (v).
- AN** - 2019-39387K
- AP** - CN20191115552 20190215
- CN** - RAY60P-K RAY60P-P RA1KPK-K RA1KPK-P R06313-K R06313-P R01714-K R01714-S R01678-K R01678-S R01510-K R01510-S
- CPY** - CAO-H-I; XIAN-I
- DC** - C04

DCR	- [1] 1845865 CL PRD; 275111 CL PRD; 2923 CL PRD; 7 CL RCT; 127 CL RCT; 157 CL RCT
DR	- 1714-S 1678-S 1510-S
DW	- 201948
IC	- C05D1/00; C05D11/00; C05D5/00
IN	- CAO H; XIA N
INW	- CAO H; XIA N
IW	- PREPARATION POTASSIUM HYDROGEN SULPHATE FERTILISER INDUSTRIAL WASTE SULPHURIC ACID COMPRISE REACT CHLORIDE ADD HOT WATER DILUTE NEUTRALISE COOLING SEPARATE
IWW	- PREPARATION POTASSIUM HYDROGEN SULPHATE FERTILISER INDUSTRIAL WASTE SULPHURIC ACID COMPRISE REACT CHLORIDE ADD HOT WATER DILUTE NEUTRALISE COOLING SEPARATE
M2	- [01] A212 A940 A950 C101 C108 C316 C540 C550 C730 C801 C802 C804 C805 M411 M720 M904 M905 N200 N513 P112; RAY60P-K RAY60P-P - [02] A212 A940 C108 C316 C540 C730 C801 C802 C803 C804 C805 M411 M720 M904 M905 N200 N513 P112; RA1KPK-K RA1KPK-P - [03] A119 A940 C101 C108 C316 C540 C730 C801 C802 C804 C805 M411 M720 M904 M905 N200 N513 P112; R06313-K R06313-P - [04] C101 C108 C316 C540 C730 C800 C801 C802 C804 C805 M411 M730 M904 M905 M910; R01714-K R01714-S - [05] A119 A940 C017 C100 C730 C801 C803 C804 C805 C806 C807 M411 M730 M904 M905 M910; R01678-K R01678-S - [06] A212 A940 C108 C550 C730 C801 C802 C803 C804 C805 C807 M411 M730 M904 M905 M910; R01510-K R01510-S
MC	- C05-A01 C05-C05 C14-T03
NC	- 1
NPN	- 1
OPD	- 2019-02-15
PA	- (CAOH-I) CAO H - (XIAN-I) XIA N
PAW	- (CAOH-I) CAO H - (XIAN-I) XIA N
PD	- 2019-04-19
PN	- CN109650947 A 20190419 DW201948
PR	- CN20191115552 20190215
TI	- Preparing potassium hydrogen sulfate fertilizer from industrial waste sulfuric acid comprises reacting industrial waste sulfuric acid and potassium chloride, adding into partial hot water dilution, neutralizing, cooling and separating
UPA	- 20190703
UPM	-



US007780941B1

(12) **United States Patent**
Lalancette et al.

(10) **Patent No.:** **US 7,780,941 B1**

(45) **Date of Patent:** **Aug. 24, 2010**

(54) **POTASSIUM MAGNESIUM FERTILIZER**

(75) Inventors: **Jean-Marc Lalancette**, Sherbrooke
(CA); **David Lemieux**, Thetford Mines
(CA); **Bertrand Dubreuil**,
Trois-Rivieres (CA)

(73) Assignee: **Nichromet Extraction Inc.** (CA)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) Appl. No.: **12/497,989**

(22) Filed: **Jul. 6, 2009**

(30) **Foreign Application Priority Data**

Apr. 6, 2009 (CA) 2661479

(51) **Int. Cl.**

C01D 5/12 (2006.01)

C05D 1/00 (2006.01)

C05D 5/00 (2006.01)

(52) **U.S. Cl.** **423/544**; 423/551; 423/552;
423/554; 71/31; 71/61; 71/63

(58) **Field of Classification Search** 423/544,
423/551, 552, 554; 71/31, 61, 63
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,902,344 A * 9/1959 Cevidalli et al. 423/161
3,726,965 A * 4/1973 Neitzel et al. 423/551
5,102,441 A * 4/1992 Zentgraf et al. 71/63
2002/0114759 A1 * 8/2002 Cabello-Fuentes 423/482

FOREIGN PATENT DOCUMENTS

JP 57-129823 A * 8/1982

OTHER PUBLICATIONS

Shreve, R. Norris, "Manneheim Process", *Chemical Process Industries*, Third Edition (McGraw-Hill 1967), p. 346.

* cited by examiner

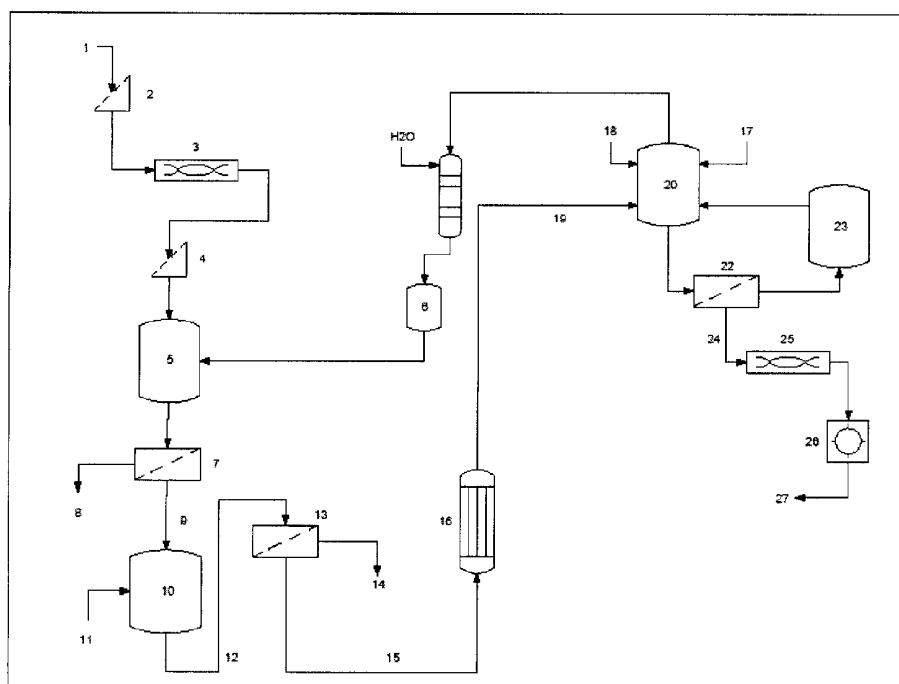
Primary Examiner—Timothy C Vanoy

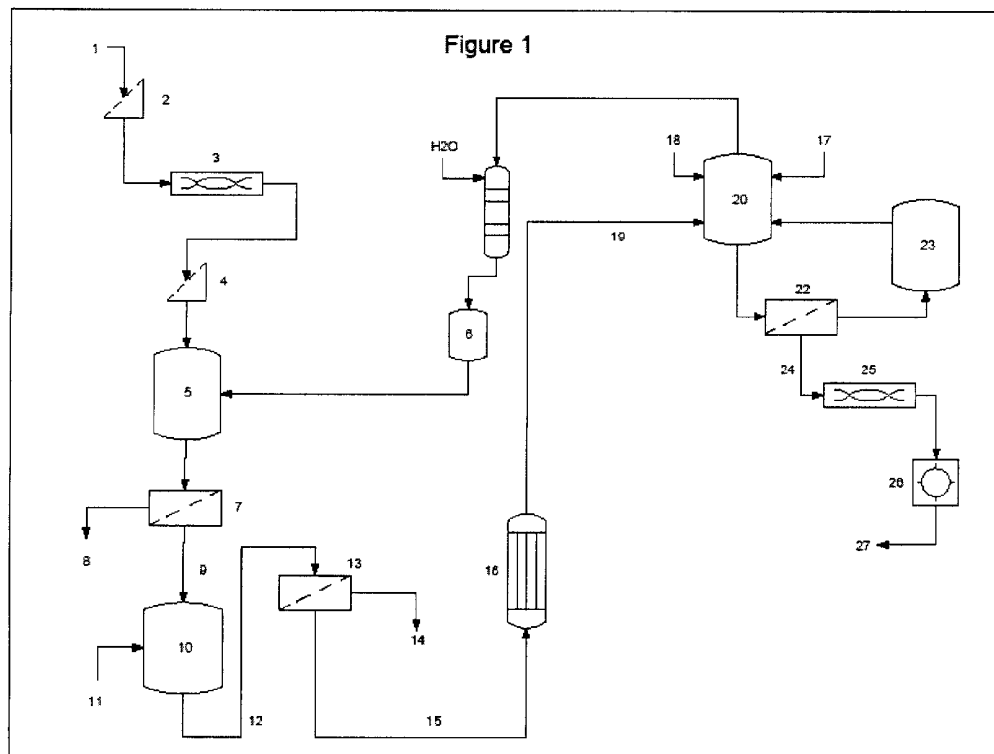
(74) *Attorney, Agent, or Firm*—Schwegman, Lundberg &
Woessner, P.A.

(57) **ABSTRACT**

A process for producing potassium magnesium sulfate, comprising reacting sulfuric acid with potassium chloride and magnesium chloride at a temperature in a range comprised between about 100 and about 160° C., thereby producing potassium magnesium sulfate and hydrochloric acid, the sulfuric acid being reacted with potassium chloride and magnesium chloride simultaneously or sequentially.

34 Claims, 1 Drawing Sheet





1

POTASSIUM MAGNESIUM FERTILIZER

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority on Canadian application serial No. 2,661,479, filed on Apr. 6, 2009. All documents above are incorporated herein in their entirety by reference.

FIELD OF THE INVENTION

The present invention relates to fertilizers. More specifically, the present invention is concerned with production of potassium magnesium sulfate.

BACKGROUND OF THE INVENTION

On the one hand, potassium magnesium sulfate (SOPM) is a very desirable fertilizer used in intensive agriculture, incorporating three agronomic elements: potassium, magnesium and sulfur. However, as a mined product, SOPM not only is found in diminishing quantities, but also has a chlorine content of one to several percent, which reduces its efficiency in agricultural applications. A synthetic approach allowing nearly chlorine-free SOPM would therefore ensure high quality supplies and intensive uses without the sterilizing effect of chloride on soils.

It is known to generate hydrochloric acid from the action of sulfuric acid on a chloride. At temperatures in the range between 100 and 160° C., the reaction of sulfuric acid with potassium chloride (potash) leads to hydrochloric acid and an acid potassium sulfate, KHSO₄, as follows:



In order to achieve the complete substitution of potassium for both hydrogens on the sulfuric acid, much higher temperatures are required, in the range of 400° C., as well noted in the art (Mannheim process, Chemical Process Industries, R. N. Shreeve, McGraw-Hill, 3rd ed., 1967, p. 346). At this temperature, HCl is obtained together with potassium sulfate K₂SO₄ as follows:



As people in the art will appreciate, such a high temperature reaction leads to severe corrosion problems, difficult heat transfer and large energy consumption.

Therefore, there is a need in the art for a method to overcome the above-mentioned shortcomings.

SUMMARY OF THE INVENTION

More specifically, there is provided a process for producing potassium magnesium sulfate, comprising reacting sulfuric acid with potassium chloride and magnesium chloride at a temperature in a range comprised between about 100 and about 160° C., thereby producing potassium magnesium sulfate and hydrochloric acid.

Other objects, advantages and features of the present invention will become more apparent upon reading of the following non-restrictive description of embodiments thereof, given by way of examples only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

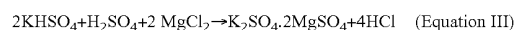
In the appended drawings:

FIG. 1 is a schematic diagram of a method according to an embodiment of an aspect of the present invention.

2

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

In a first aspect of the present invention, it is shown that a complete substitution of the hydrogen of sulfuric acid by potassium and magnesium can be done by reacting potassium hydrogen sulfate in a range of temperatures between 100 and 160° C. with magnesium chloride, as follows:



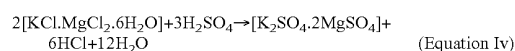
In this reaction, a complete combination of the sulfuric acid with potassium and magnesium in the form of chlorides occurs at atmospheric pressure. Potassium hydrogen sulfate (KHSO₄) reacts with magnesium chloride, yielding hydrochloric acid HCl which is removed from the system as soon as it is formed to be absorbed in water.

Equation III applies in a temperature range between 100 and 160° C. Temperatures between 140 and 160° C. allow faster reactions.

This reaction of sulfuric acid with both chlorides can be sequential, wherein sulfuric acid first reacts with KCl to yield potassium hydrogen sulfate, and then with MgCl₂ in order to yield SOPM, as happens in the reaction described by Equation III above (see example 1 below).

Alternatively, the reaction of sulfuric acid with both chlorides can be simultaneous, using a mixing of these chlorides, which occurs naturally in carnallite, or which is produced for that purpose.

A natural source of chlorides of potassium and magnesium, such as carnallite [KCl.MgCl₂.6H₂O] for example, may be used in order to obtain a complete reaction with sulfuric acid, under the same range of mild temperatures of around 100 to 160°, as follows:



Thus, hydrochloric acid is generated by the action of sulfuric acid on the chlorides KCl and MgCl₂ (see example 2 below).

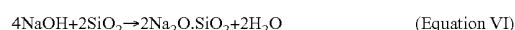
Such hydrochloric acid may be sold as such.

Moreover, as well known in the art, hydrochloric acid may be used to digest mineral ores, such as serpentine [3MgO.2SiO₂.2H₂O] for example, as follows:



More precisely, the acid digestion of serpentine with hydrochloric acid yields a crude solution of magnesium chloride contaminated by significant amounts of chlorides of the base metals present in the starting serpentine ore, namely, iron, nickel and chromium. This crude MgCl₂ solution may be purified by controlled pH adjustment and filtration of the precipitated transition metals oxides, or hydroxides. This mixture of oxides, because of its nickel and chromium components, can in turn be readily used in metallurgical operations.

It is to be noted that, besides the crude solution of magnesium chloride discussed hereinabove, the leaching of the serpentinic ore leaves an insoluble solid, mostly deprived of magnesium and base metals (see Equation V). Silica (SiO₂) is the main component of this solid, as shown in Equation V above, in the temperature range between 100 and 160° C. This silica being the result of chemical leaching, it possesses a very high propensity to dissolution in caustic NaOH as follows:



This last reaction, which is done at about 230° C. under pressure in an autoclave, produces a concentrated solution of sodium orthosilicate or waterglass [2Na₂O.SiO₂] (see

example 5 below). Thus, due to the high reactivity of the silica resulting from the acid leaching of the serpentinitic ore, sodium orthosilicate can be obtained under mild conditions, without the necessity to use fusion of silica with soda ash at 1200° C. as currently practiced to obtain waterglass for example.

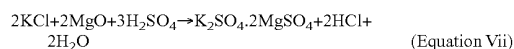
As shown by Equations III and IV, the reaction of the sulfuric acid with potassium and magnesium chlorides also yields, besides HCl, potassium magnesium sulfate $[K_2SO_4 \cdot 2MgSO_4]$ (SOPM). Therefore, SOPM can be synthesized by these reactions, which take place at low temperature, in the range between 100 and 160° C. Independently of the sources of KCl and $MgCl_2$ (see examples 1 and 2 below), SOPM with a potassium to magnesium ratio of 2K/2 Mg is obtained (Langbeinite, $[K_2SO_4 \cdot 2MgSO_4]$), together with a corresponding production of HCl that can be sold as such, or used for mineral leaching as shown above.

In order to insure the neutral character of the produced SOPM, a small amount of MgO can be added to the reaction mixture in Equation III. Moreover, the K/Mg ratios can be adjusted by adding further amount of MgO, thereby yielding equivalent SOPM such as shönite $[K_2SO_4 \cdot MgSO_4]$ (2K/1Mg ratio) if needed or other K/Mg ratios, if desired.

Moreover, indirectly, SOPM can be produced from the digestion of serpentine, since, as shown in Equation V, it produces magnesium chloride $MgCl_2$. This magnesium chloride $MgCl_2$ may be used to achieve a complete neutralization of sulfuric acid into hydrochloric acid HCl, as shown above in Equations 3 and 4 (see examples 1 and 2 below). Alternatively, the produced magnesium chloride can be recovered either in the form of a solution or as a solid hexahydrate $[MgCl_2 \cdot 6H_2O]$.

In still a further embodiment, exemplified in Example 6 below, SOPM is fabricated using digestion of laterite (see Equation V). Laterites are silicates of serpentinitic origin with a Ni content in the range between 0.5 and 2% Ni. In this case, the recovery of nickel is significant, as compared to when leaching serpentine.

In still a further embodiment, exemplified in Example 3 below, SOPM is fabricated using magnesium oxide MgO as a source of magnesium, as follows:



Therefore, the present method, by involving the reaction of sulfuric acid with a multiplicity of ions (K, Mg) rather than potassium singly (see Equations II, IV and VII), allows producing SOPM, at relatively low temperature and with the avoidance of the extremely corrosive conditions of other techniques such as the Mannheim process (see Equation II).

In a system according to an embodiment of another aspect of the present invention, illustrated by the diagram of FIG. 1, serpentinitic tailings (1) are circulated through a grizzly (2) in order to remove rocks larger than two inches. The resulting finer fraction is dried in a rotary dryer (3) and classified through a 14 mesh screen (4). The minus 14 mesh material is admitted to a leaching reactor (5), along with 32% hydrochloric acid (6). The charge is stirred at 100° C. for one hour, and filtrated through a belt filter (7), the insoluble fraction (8) being mostly silica and the filtrate (9), a crude solution of magnesium chloride.

This crude solution is purified in a stirred precipitator (10) by controlled addition of basic calcined magnesia (11). The resulting slurry from the precipitator (12) is directed to a filter (13), where the mixture of iron, nickel and chromium oxides/hydroxides (14) is separated from the cleaned stream of magnesium chloride (15). The concentration of the magnesium

chloride is then increased from 20% to 30% $MgCl_2$, by partial evaporation of the stream in an evaporator under vacuum (16).

In parallel with this production of magnesium chloride, silica and base metals oxides/hydroxides, the preparation of SOPM is achieved in a stirred and heated reactor (20), by admission in said reactor of sulfuric acid (17), potash (18) and magnesium chloride (19), in such proportion as to obtain the desired ratio of potassium, magnesium and sulfate in the end product. After a contact time of one hour at 100 to 160° C., the mass is taken up by a saturated brine obtained from previous runs (21), and filtered over a belt filter (22). The saturated brine is stored for further use (23), and the wet sulfate of potassium and magnesium is dehydrated in a dryer (25) and agglomerated in a pelletizing circuit (26), to give the expected particulates of SOPM at the required dimensions (27) for agricultural uses.

Thus, SOPM fertilizer is produced and it has a very low content of chlorine, typically less than 1%, and even less than 0.5%, and incorporates other desirable agronomic elements, magnesium and sulfur, as well known in the art.

The excess magnesium chloride, along with reactive silica and precipitated mixture of base metals oxides/hydroxides, have been found to be useful and negotiable products, particularly the reactive silica after its transformation into waterglass.

Still in FIG. 1, in a separate circuit, the insoluble fraction (8) can be treated in an autoclave with a sodium hydroxide solution at 230° C. to give, after filtration, a solution of sodium silicate.

The present system and method therefore allow a complete reaction of the sulfuric acid (both hydrogens) with potassium and magnesium in the form of chlorides, at relatively low temperatures in the range between 100 and 160° C., which is unexpected in view of the Mannheim process (Equation II), where the substitution of two potassium on the sulfate group requires temperatures of at least 400° C. with very severe problems and limitations, as indicated above.

Moreover, the present system and method therefore allow synthesizing SOPM at relatively low temperatures in the range between 100 and 160° C.

The following examples are presented to illustrate the invention.

In Example 1, production of hydrochloric acid and SOPM is achieved by placing: 77 Kg of 93% sulfuric acid in a glass-lined reactor of two cubic meters heated by a steam jacket and equipped with a stirrer. The system is heated to 160° C. with 100 psi steam in the jacket. Then, 38 Kg of KCl are introduced in the reactor, with stirring. This addition is accompanied by HCl gas evolution (see Equation I). This stream of HCl is directed to an adsorption unit where 32% HCl is formed. After a contact time of 30 minutes, the HCl evolution has subsided and the reaction is completed by addition of 150 Kg of an $MgCl_2$ solution at 28% $MgCl_2$. There is a second evolution of HCl, which is completed after 1 1/2 hour. At this point, mother liquors from previous runs are used to carry out the reaction mass which is filtered and finally dried at 200° C. Thus 107.6 Kg of synthetic langbeinite material, $K_2SO_4 \cdot 2MgSO_4$ are obtained.

In Example 2, carnallite is reacted with sulfuric acid. A portion of 151.4 g of a 40% w/w carnallite solution is reacted with 34.4 g of a 93% w/w sulfuric solution in a glass container. This mixture is heated for 1 hour at 100-140° C. The water and HCl gas are evaporated, creating a weight loss of 23.6 g HCl and 110.44 g of water. The solid is recovered and dried overnight at 200° C. 45.72 g of solid were collected, containing 5.69 g of Mg, 8.70 g of K and 31.33 g of sulfate.

The composition of the solid is very close to the langbeinite formula $[K_2SO_4 \cdot 2MgSO_4]$, with 12.44% Mg, 19.03% K and 68.5% SO_4 .

In Example 3, potash KCl and magnesium oxide MgO are reacted: a portion of 30.1 g of KCl is reacted with 60.4 g of sulfuric acid 98% in a glass container. This mixture is heated for 30 min. at 110-150° C. followed by addition of 16.2 g of MgO and heating for another 30 min. The water and HCl are evaporated, and then the solid is recovered and dried. 83.9 g of solid are collected, containing 8.2 g of Mg, 16.0 g of K and 58.3 g of sulfate. The composition of the solid is very close to the langbeinite formula, with 9.8% Mg, 19.1% K, 69.5% SO_4 , 0.2% Cl and 0.6% water-insoluble material.

In Example 4, serpentine is digested with hydrochloric acid as follows: in a 1.5 cubic meters reactor equipped with a stirrer, a mass of one cubic meter of water is heated to 90° C. with steam in order to warm the reactor. This heating water is dumped. Then 285 Kg of HCl 32%, preheated to 60° C., are introduced into the reactor. A serpentinic material (111 Kg), 100% less than 16 mesh, 10% free moisture, is added with stirring to the warm acid.

The reaction is exothermic and the temperature remains at 85° C. for a period of one hour. The reaction slurry is treated with a flocculent, ten liters of organopole 6405, at a concentration of 0.375%. The filtration is done on a belt filter 18" wide with two rinsing zones. The filtrated pulp has a weight of 135 Kg with a water content 50%. The solution including the rinsings has a volume of 390 l. The analysis of the liquid phase indicates a recovery of 89% of the magnesium in the starting serpentine ore, of 94% of the iron, 88% of the nickel and 78% of the chromium. The pH of this solution is 0.7.

In order to purify the magnesium chloride solution, the pH of the solution is raised to 5.0 with basic calcined magnesium oxide. The precipitated oxides/hydroxides are flocculated with organopol 6404 and filtered over a belt filter 18" wide. The solution thus obtained, 400 liters, contains magnesium chloride at a concentration of 20%. The filtrated pulp, made essentially of oxides/hydroxides of iron, chromium and nickel, weighs 15 Kg with a moisture content of 50%.

Example 5 illustrates the formation of sodium silicate from silica residue produced as a result of serpentine leaching. In a 300 ml autoclave 10 g of a crude insoluble fraction, 15 g of NaOH and 15 g of water are placed. The autoclave is heated to 200-240° C. for a period of 3½ hours. The corresponding pressure is 120 psi. After this reaction, the pressure is released after cooling and the resulting solution is filtered to remove insolubles. The filtrate contains 3.7 g of silica, as measured by acidification and purification.

Using a procedure similar to Example 4 of digestion of serpentine with HCl, Example 6 describes digestion of laterite with hydrochloric acid: 150 Kg (20% moisture) of a laterite (having the following composition: 2.2% Ni, 12.9% Fe and 10.0% Mg) is treated with 158 Kg of HCl 32%. After the usual procedure, the recovery of leached nickel is 93%, iron 73% and magnesium, 84%. Procedures known to those familiar with the art allow the isolation of nickel from the FeMgNi solution, such as with ion exchange resins.

Although the present invention has been described hereinabove by way of embodiments thereof, it may be modified, without departing from the nature and teachings of the subject invention as defined in the appended claims.

What is claimed is:

1. A process for producing potassium magnesium sulfate, comprising reacting sulfuric acid with potassium chloride

and magnesium chloride at a temperature in a range between about 100 and about 160° C., thereby producing potassium magnesium sulfate and hydrochloric acid.

2. The process of claim 1, wherein the sulfuric acid is simultaneously reacted with the potassium chloride and the magnesium chloride.

3. The process of claim 1, wherein the sulfuric acid is reacted with the potassium chloride and the magnesium chloride sequentially.

4. The process of claim 3, wherein the sulfuric acid is reacted with the potassium chloride, thereby producing potassium hydrogen sulfate; and then the magnesium chloride is added, thereby yielding potassium magnesium sulfate.

5. The process of claim 1, wherein the potassium chloride is in the form of potash.

6. The process of claim 1, wherein at least part of the magnesium chloride is produced by acid leaching of a serpentine ore or a laterite ore with hydrochloric acid.

7. The process of claim 1, wherein at least part of the magnesium chloride is in the form of a 30% magnesium chloride in water.

8. The process of claim 1, wherein at least part of the magnesium is provided by reacting sulfuric acid with magnesium oxide.

9. The process of claim 8, wherein the reaction of sulfuric acid with magnesium oxide is subsequent to the reaction of sulfuric acid with potassium chloride.

10. The process of claim 8, further comprising adjusting a K/Mg ratio of the potassium magnesium sulfate by adding magnesium oxide to the potassium chloride and magnesium chloride.

11. The process of claim 2, wherein said at least part of the potassium chloride and at least part of the magnesium chloride are in the form of carnallite.

12. The process of claim 11, wherein the carnallite is in solution in water.

13. The process of claim 1, wherein the potassium magnesium sulfate has a K/Mg ratio of 2:2.

14. The process of claim 1, wherein the potassium magnesium sulfate has a K/Mg ratio of 2:1.

15. The process of claim 1, wherein the potassium magnesium sulfate comprises less than about 1% of chlorine impurity.

16. The process of claim 1, wherein the potassium magnesium sulfate comprises less than about 0.5% of chlorine impurity.

17. The process of claim 1, wherein the sulfuric acid is an acid at 92 to 98% H_2SO_4 .

18. The process of claim 17, wherein the sulfuric acid is an acid at 92 to 94% H_2SO_4 .

19. The process of claim 1, comprising preheating the sulfuric acid to a temperature in the range between 100° C. and 160° C.

20. The process of claim 1, wherein the sulfuric acid is reacted with the potassium chloride and the magnesium chloride at a temperature between about 100° C. and about 160° C.

21. The process of claim 1, wherein the sulfuric acid is reacted with the potassium chloride and the magnesium chloride at a temperature between about 140° C. and about 160° C.

22. The process of claim 20, wherein the sulfuric acid is reacted with the potassium chloride and the magnesium chloride during three hours.

23. The process of claim 1, further comprising adsorbing the hydrochloric acid in water.

24. The process of claim 23, wherein said adsorbing yields a 30 to 35% hydrochloric acid solution.

7

25. The process of claim 1, further comprising recovering excess magnesium chloride in the form of a solution or a hexahydrate.

26. The process of claim 1, further comprising using the hydrochloric acid to leach a serpentine ore, thereby producing a reaction mixture comprising silica and a mixture of chlorides of magnesium, iron, nickel and chromium.

27. The process of claim 26, wherein the leaching is at a temperature between about 90° C. and about 110° C.

28. The process of claim 27, wherein the serpentinitic ore comprises between about 35 and about 41% weight of magnesium oxide.

29. The process of claim 28, further comprising filtering the reaction mixture, thereby producing a liquid portion and a solid portion.

30. The process of claim 29, further comprising recovering the magnesium chloride from the liquid portion.

8

31. The process of claim 30, wherein the magnesium chloride is recovered from the liquid portion as a 20 to 30% magnesium chloride solution in water.

32. The process of claim 31, wherein said magnesium chloride recovered from the liquid portion is a magnesium chloride produced by acid leaching of a serpentine ore with hydrochloric acid.

33. The process of claim 30, further comprising:

i. recovering the silica from the solid portion; and

ii. dissolving the recovered silica in caustic at a temperature of about 230° C. under pressure, thereby producing sodium orthosilicate and waterglass.

34. The process of claim 1, further comprising using the hydrochloric acid to leach magnesium oxide from a laterite ore.

* * * * *