

CASTELLANOS & Co.
A B O G A D O S
Calle 94 A No. 7 A - 09
Bogotá, D.C., COLOMBIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 06-053243- -00005-0000

Fecha: 2011-02-01 14:12:16 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALI
Act. 444 RESPUESTAREQUE Folios: 13

Señor

Jefe de la División de Nuevas Creaciones

Superintendencia de Industria y Comercio

Ministerio de Comercio, Desarrollo Industria y Turismo

E. S. D.

Re.: Expediente No. **06.053.243**

Solicitud del examen de patentabilidad correspondiente a la Patente PCT Entrada en Fase Nacional, para:

"INHIBIDORES DE CORROSION PARA FORMULACIONES PESTICIDAS ACUOSAS"

Solicitante: **SYNGENTA PARTICIPATIONS AG**

RESPUESTA A EXAMEN DE FONDO

MARGARITA CASTELLANOS ABONDANO, mayor de edad, identificada y domiciliada como aparece al pie de mi firma, en atención a su oficio No. 14768 notificado el 12 de noviembre de 2010, atentamente me permito dar repuesta al mismo de la siguiente manera:

Ante la observación del examinador:

"El título de la invención debe ser modificado y definir específicamente el objeto de la invención"

El solicitante presenta el siguiente título:

INHIBIDORES DE CORROSION PARA FORMULACIONES PESTICIDAS ACUOSAS QUE COMPRENDEN UN ADITIVO DE SAL IONICA DE NITRATO

"El capítulo reivindicatorio es presentado en un lenguaje muy amplio y no define específicamente el alcance de la invención. Así por ejemplo, expresiones como "al menos", una cantidad, optativamente, inferior o igual" son muy amplias y no definen el objeto de la invención.

Nótese que en el capítulo descriptivo se divulga un único ingrediente activo para el cual se demuestra un efecto. No obstante dicho ejemplo es insuficiente para respaldar la amplia generalización presentada en el capítulo reivindicatorio "5-90% en peso de al menos un pesticida". El solicitante debe limitar el alcance de su invención.

Por último sírvase suprimir la frase "...efectiva para reducir la corrosión de superficies metálicas" puesto que es explicativa, hace referencia al problema técnico, es decir caracteriza la composición por el objetivo a alcanzar y no define ninguna característica técnica de la composición"

Ante estas objeciones, el solicitante presenta un nuevo pliego reivindicatorio, en el cual las reivindicaciones 1 y 7 se han combinado, la reivindicación 1 ha sido limitada a aquellas composiciones donde el pesticida es mesotriona, o una sal agriculturalmente aceptada o un quelato de metal del mismo. La reivindicación 1 ha sido además modificada para indicar que el aditivo de sal iónica de nitrato está presente en el concentrado pesticida en un rango de 0.001 % a 10 % en peso, el cual se encuentra sustentado en la página 4, línea 1 de la publicación de la solicitud.

Reivindicaciones relativas a un uso o a un segundo uso

"La reivindicación 13 hace referencia al uso de una sal de nitrato sódico, lo cual de acuerdo con el artículo 14 no es patentable pues no corresponde a una invención de producto ni de procedimiento.

Así mismo, el método de la reivindicación 12 hace referencia simplemente al uso de la composición pesticida de interés para el control selectivo de plagas en cultivos de plantas útiles"

Ante estas objeciones, las reivindicaciones 12 y 13 han sido eliminadas.

Nivel inventivo

"Al comparar el concentrado de esta solicitud con las composiciones de D1 (US5416061) se observa que dicho concentrado contiene una sal de nitrato, lo cual produce la inhibición de la corrosión en superficies metálicas.

En contraste, el documento D2 (WO99/07918), enseña claramente que una sal inorgánica de nitrato es especialmente útil como inhibidor de la corrosión en superficies metálicas que tienen contacto con fluidos acuosos.

En consecuencia, para un técnico medio en la materia, teniendo en cuenta las enseñanzas del estado de la técnica en su totalidad, sería obvio incluir el inhibidor de la corrosión de D2 justamente para inhibir la corrosión de las superficies metálicas"

En D1 se muestra una composición herbicida que comprende (a) bromoxinil y (b) un derivado de 2-benzoilciclohexano-1,3-diona de Formula (I). A pesar que D1 puede sugerir que la composición puede además comprender un inhibidor de corrosión, no hay sugerencia que este inhibidor sea una sal iónica de nitrato.

D2 por su parte, se refiere al uso de sales de nitrato de metal alcalino, por ejemplo nitrato de sodio, para inhibir la corrosión de superficies metálicas presentes en los sistemas de enfriamiento de motores de combustión interna.

Debe notarse que D2 se refiere a un campo técnico distinto de D1, y una persona con conocimiento del arte apreciara en vista de las otras referencias del arte previo que un inhibidor de corrosión que es eficaz en un sistema no es necesariamente efectivo en otro.

Por ejemplo, US 5376159 (copia adjunta) enseña que la corrosión al acero dulce puede ser causada por soluciones concentradas de fertilizante nitrogenado, tal como el nitrato de amonio urea, y que esta corrosión puede ser reducida por el uso de cantidades de traza de molibdato (nótese que con respecto a esta invención puede verse que el molibdato no

CASTELLANOS & Co.
A B O G A D O S
Calle 94 A No. 7 A - 09
Bogotá, D.C., COLOMBIA

parece ser compatible con respecto a los concentrados conteniendo mesotriona que son objeto de las reivindicaciones de acuerdo con las presentes modificaciones.

Como puede observarse de la tabla provista en la página 14 de la descripción de la presente solicitud, el uso de molibdato de sodio (muestra 6) en conexión con una solución que contiene mesotriona generó un aumento de peso, probablemente debido al enchapado cobre de la composición. Por consiguiente, una consideración adecuada del arte previo revela que la elección de un inhibidor de corrosión para un sistema particular no es predecible como el examinador parece intentar sugerir. Ciertamente, no existe una tendencia consistente con respecto al uso de nitratos como inhibidores de corrosión. Por ello, se considera que una persona del arte enfrentada al problema de proporcionar un inhibidor de corrosión para concentrados de mesotriona no hubiese considerado las enseñanzas de D1 y D2.

Dados los argumentos del solicitante y las modificaciones realizadas, solicito a su Despacho continuar el trámite de la presente invención toda vez que las objeciones planteadas por su Despacho han sido superadas.

Del Señor Jefe,


Margarita Castellanos Abondano
C.C. No. 39.779.654 de Usaquén
T.P.A. No. 70.819 de C.S.J.
Calle 94 A No. 7 A-09 – Bogotá, D.C.
Tel.: 7560770

Bogotá, D.C. **1 FEB. 2011**

Memorial de respuesta a examen de fondo/P1361



Industria y Comercio

SUPERINTENDENCIA

Espacio reservado para el adhesivo de radicación

FORMULARIO ÚNICO DE CORRECCIONES Y MODIFICACIONES

①

SOLICITUD DE:



Corrección de Error Material



Modificación a una solicitud

②

Nombre: SYNGENTA PARTICIPATIONS AG

Dirección: Schwarzwaldallee 215, CH-4058
Basilea - SUIZA

Nacionalidad o Domicilio: Basilea - SUIZA

Lugar de Constitución: Basilea - SUIZA

Teléfono:

Fax:

E-mail:

IDENTIFICACIÓN

C.C.



NIT



C.E.



Otro



Cual

Número

③

REPRESENTANTE
O APODERADO

Nombre: MARGARITA CASTELLANOS A.

Dirección: Calle 94 A No. 7 A-09

Teléfono: 756 0770 Fax: 755 0158

E-mail: info@castellanosyco.com

IDENTIFICACIÓN

C.C.



NIT



C.E.



Otro



Cual

Número

39'779.654

TPA

70,819

④

Número de Expediente:

06.053.243

⑤

Descripción de la corrección o modificación solicitada:

Presento un nuevo capítulo reivindicatorio al cual solicito se realice examen de patentabilidad

⑥

Comprobante de pago No.

11-004850

Fecha

18 de enero de 2011

⑦

Anexos:



Comprobante de pago de la tasa.



Poderes si fuere el caso, junto con la sustitución de los mismos a mi favor.



Documento que acredita la existencia y representación legal de las partes, cuando sean personas jurídicas



Nuevo capítulo reivindicatorio

⑧

NOMBRE

MARGARITA CASTELLANOS A.

FIRMA

Margarita Castellanos A.
CC 39'779.654 Usaqué - TPA 70.819 CSJ

Instrucciones para el diligenciamiento del presente formulario, ver reverso de esta página - P1361

- 1 FEB. 2011

5

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -

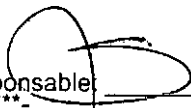
 Industria y Comercio SUPERINTENDENCIA	RECIBO DE CAJA	No. 11 - 004850
		Bogotá D.C., 18 de 2011 - 14:14:29

RECIBIDO DE : CASTELLANOS Y Y CO NI 800.174.641

*** Soporte del Pago ***					
TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR PAGO
CONSIGNACION	BANCO DE BOGOTA	062754387	387633750	18/01/2011	17.501.920.00

*** Conceptos Pagados ***			
CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO Vr.CONCEPTO
1	50005-01-03 CAMBIO DE MODALIDAD Y MODIFICACIONES	EN N.CREACION CORRECCION A SOLICITUD EN TRAMITE / MODIFICA	118.000.00 118.000.00
			\$118.000.00
			=====

SON: **CIENTO DIECIOCHO MIL PESOS MONEDA CORRIENTE**

Responsable: 

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 06-053243- -00005-0000
Fecha: 2011-02-01 14:12:16 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALI
Act. 444 RESPUESTAREQUE Folios: 13

REIVINDICACIONES

1. Un concentrado pesticida que comprende:

- a) 2-85% en peso de agua
- b) 5-90% en peso del pesticida mesotriona, o una sal agriculturalmente aceptable o un quelato de metal de la misma,
- c) 0.001% a 10% en peso de aditivo de sal de nitrato iónica efectiva para reducir la corrosión de superficies metálicas
- d) optativamente, otros auxiliares de formulación

en donde la relación del componente c) al componente b) es inferior o igual a 0,3:1.

2. El concentrado de la reivindicación 1 en donde el pH de la composición es 6 o inferior.

3. El concentrado de la reivindicación 1 en donde el pesticida está en la forma de una sal o quelato metálico.

4. El concentrado de la reivindicación 1 que comprende al menos un auxiliar de formulación en la forma de una sal.

5. El concentrado de la reivindicación 4 en donde el auxiliar de formulación en la forma de una sal comprende al menos un cloruro de metal alcalino o de metal alcalino térreo.

6. El concentrado de la reivindicación 1 en donde la sal de nitrato iónica comprende nitrato de amonio.

7. El concentrado de la reivindicación 1 en donde el pesticida comprende un quelato de cobre o zinc de mesotriona.

8. Una composición pesticida obtenida mediante la dilución de un concentrado de acuerdo con la reivindicación 1 en una cantidad de portador adecuada.

9. Una composición pesticida de acuerdo con la reivindicación 8 en donde el portador es agua.



US005376159A

United States Patent [19]

[11] Patent Number: 5,376,159

Cunningham et al.

[45] Date of Patent: Dec. 27, 1994

[54] CORROSION INHIBITOR FOR NITROGEN FERTILIZER SOLUTIONS

[75] Inventors: Raymond T. Cunningham, Sugar Land; Kristen T. Moore, Houston, both of Tex.

[73] Assignee: Nalco Chemical Company, Naperville, Ill.

[21] Appl. No.: 119,960

[22] Filed: Sep. 10, 1993

[51] Int. Cl.⁵ C05C 1/00; C05C 9/00; C05C 13/00

[52] U.S. Cl. 71/30; 71/DIG. 4; 423/269; 252/389.54

[58] Field of Search 71/30, DIG. 4; 423/269; 252/389.54

[56] References Cited

U.S. PATENT DOCUMENTS

3,024,100 3/1962 Langguth et al. 71/34
3,617,240 11/1971 Scott, Jr. et al. 71/29

FOREIGN PATENT DOCUMENTS

865038 3/1971 Canada .

OTHER PUBLICATIONS

Derwent Abstract 78-57487A, Takayaso, "Preventing . . . Molybdate to the Water", 1978.

Derwent Abstract 71-17057S, Allied, "Non-corrosive Fertilizer Solutions", 1967.

CA114 (1):5379n; Physicochemical study of a urea-ammonium nitrate solution containing trace elements; Kosyakov, N. E., Kolyada, M. S., Poyarkova, I. F., Sergienko, I. D.; USSR; 1990.

CA103(19):159722d; Liquid molybdenum-nitrogen fer-

tilizers; Lubis, B., Sviklas, A., Padvaiskas, I.; USSR; 1985.

CA96(17):141787f; Stabilization of nitrogenous fertilizer solutions based on ammonium nitrate and urea; Plasil, Jiri, Kraft, Jaroslav; 1982.

CA92(23):197128b, Effect of microadditives on the physicochemical properties and corroding activity of liquid complex fertilizers based on polyphosphoric acid; Bugai, P. M., Slyn'ko, V. P., Akhtyrskaya, A. A., Makarov, V. A.; 1977.

CA90(11):85942q; Fertilizers solutions; Michaud, Horst, Rieder, Georg, Seeholzer, Joseph; 1978.

CA86(11):70783g; Development of liquid multicomponent fertilizers based on potassium and ammonium nitrates and diphosphates, urea, and water; Endovitskaya, M. R.; Vereshchagina, V. I., 1974.

CA78(12):78878x; Inhibition of steel-3 corrosion in a solution of a concentrated liquid fertilizer; Osipov, A. K.; USSR; 1971.

Primary Examiner—Ferris Lander

Attorney, Agent, or Firm—Robert A. Miller; James J. Drake

[57]

ABSTRACT

A trace amount of a molybdate is disclosed for inhibiting corrosion by concentrated urea-ammonium nitrate fertilizer solutions (UAN) in contact with ferrous metal piping and equipment surfaces. From 10 to 200 ppm of sodium molybdate are blended in a UAN solution containing 20-50 weight percent water for effectively inhibiting corrosion. The corrosion-inhibited UAN solution is non-sludging, non-foaming and essentially free of precipitates.

12 Claims, No Drawings

CORROSION INHIBITOR FOR NITROGEN FERTILIZER SOLUTIONS

FIELD OF THE INVENTION

This invention relates to a corrosion inhibitor for nitrogen fertilizer solutions, and more particularly to inhibiting corrosion by urea ammonium nitrate solutions.

BACKGROUND OF THE INVENTION

Nitrogen solutions represent an important class of fertilizers. A commercially popular nitrogen fertilizer solution is made from urea and ammonium nitrate, often referred to as UAN. The UAN does not need to be kept under pressure, and can be applied directly for agricultural purposes.

The production of UAN solutions is straightforward, comprising blending urea solution, ammonium nitrate solution and any additional water in a mixing tank, in either a batch or a continuous process. Ammonia is sometimes also added to adjust the pH. Mixtures of ammonium nitrate and urea have much greater solubility as compared to that of either material alone. The UAN can be made with as little as 20% by weight water, but more typically contains 30-40% water by weight. The economics of such solutions are relatively attractive in comparison to solids because evaporation is decreased and granulation, drying and conditioning are not necessary.

One problem that has been persistent in the production, storage, transportation and use of UAN has been that the UAN liquid is extremely corrosive to steel piping systems. Without adequate corrosion inhibition, UAN solutions in ferrous tanks or piping systems will become colored within a matter of hours, usually orange or reddish indicating iron corrosion. Filmers have been used to inhibit corrosion, but these suffer from numerous problems. Where the filmer is poorly dispersed in the UAN solution, sludge can be seen as a ring on sample bottles and forms an undesirable buildup in piping and tank bottoms and walls. The use of a dispersant to avoid the sludge problem can cause the UAN solution to foam. Anti-foam additives generally become less effective with time, so the foaming problem can be addressed initially but often will become a serious problem before or during application of the UAN solution. Also, filmers tend to be depleted as the UAN solutions are transferred through a pipeline or from tank to tank since the filmer coats the pipeline or tank surface to protect it from the UAN solution. As the filmer is used up, there is less and less left in the UAN solution for inhibiting corrosion. After the UAN solution has seen enough metal surfaces to use up all of the inhibitor, it suddenly becomes uninhibited and highly corrosive.

The selection of corrosion inhibitors for liquid fertilizer solutions is made more difficult by the presence of environmental considerations. Since the fertilizer solutions are applied to crops, for example, they must be free of compounds which are toxic to the crops being fertilized, and must also facilitate compliance with industrial hygiene standards for the personnel applying the fertilizer. Thus, fluoride compounds, as one example, are undesirable in UAN solutions because they are generally agrottoxins.

Other corrosion inhibitors which are sometimes used in boilers and cooling towers, for example, are incompatible with the relatively more severely corrosive

UAN. Borate, for example, a common rust inhibitor, is not sufficiently soluble in UAN and precipitates.

SUMMARY OF THE INVENTION

It has been found that a trace amount of a molybdate can effectively inhibit corrosion by urea-ammonium nitrate solution (UAN) of steel or other ferrous metal surfaces in contact with the UAN during storage, transport, or other processing of the UAN. UAN solutions containing an effective amount of the molybdate for corrosion inhibition are non-sludging, non-foaming and essentially free of precipitate.

Accordingly, in one aspect the present invention provides an improvement in a method for inhibiting corrosion of ferrous metal surfaces by nitrogen fertilizer solutions in contact therewith. The method generally includes the steps of blending a corrosion inhibitor with a fertilizer solution consisting essentially of urea, ammonium nitrate and a minor amount of water, and contacting the metal surfaces with the resulting blend. The improvement comprises using an effective, soluble amount less than 200 ppm, by weight of the fertilizer solution, of a molybdate, preferably an alkali metal molybdate, in the blending step. The amount of the molybdate used is preferably more than 10 ppm and less than 100 ppm by weight of the fertilizer solution. The fertilizer solution can contain from about 20 up to 50 percent by weight water, and preferably has a pH from about 7 to about 8, more preferably from 7.5 to 8. The fertilizer/molybdate blend is preferably essentially free of sludge-forming compounds, of excessive foaming characteristics and of precipitates. The alkali metal molybdate is preferably added to the fertilizer solution as an aqueous solution comprising at least 65 weight percent water.

In another aspect, the present invention provides a method for processing a liquid nitrogen fertilizer in ferrous metal equipment without excessive corrosion. The method includes the steps of blending a solution of urea, a solution of ammonium nitrate and an aqueous solution of an alkali metal molybdate, optionally with water, and recovering the blend. The blend is effectively inhibited against ferrous metal corrosion and comprises a precipitate-free, non-sludging, non-foaming fertilizer solution, containing more than 10 and less than 100 ppm of the alkali metal molybdate and from about 20 to about 50 percent water. As another step, the corrosion-inhibited fertilizer solution is passed in contact with ferrous metal surfaces. The method can also include adjusting the pH of the blend to between 7 and 8, more preferably from 7.5 to 8, with ammonia. The aqueous molybdate solution preferably comprises from 5 to 35 weight percent sodium or potassium molybdate.

The method can further include storing or transporting the inhibited fertilizer solution in ferrous metal piping or containers, then diluting the inhibited fertilizer solution with at least an equal volume of water, wherein the diluted fertilizer solution remains effectively inhibited against corrosion of ferrous metal surfaces, and then applying the diluted fertilizer solution to cropland with ferrous metal equipment.

As a further aspect, the present invention provides a corrosion-inhibited liquid fertilizer. The fertilizer is a non-sludging, non-foaming, precipitate-free solution of urea, ammonium nitrate, more than 20 and less than 50 percent water, and from 10 to 100 ppm sodium or potassium molybdate, having a pH from 7.5 to 8.0 at atmo-

spheric pressure, and essentially non-corrosive to ferrous metal surfaces.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is generally applicable to urea-ammonium nitrate fertilizer solutions (UAN). The invention is, in particular, applicable to concentrated UAN in which it is generally more difficult to inhibit corrosion than in more dilute UAN. The UAN preferably contains a minor amount of water, i.e. less than 50 weight percent, but usually at least 20 weight percent water is necessary to maintain solubility of the urea-ammonium nitrate mixture. The UAN preferably comprises from 20 up to 50 percent water, more preferably from 40 to 50 percent water by weight.

The corrosion inhibitor is a molybdate which is readily soluble in the UAN at effective concentrations for inhibiting corrosion. The molybdate is also preferably non-sludging and non-foaming. As used herein, non-sludging refers to the general absence of sludge formation from the UAN over an extended period of time, e.g. several months in a storage tank. The formation of minor amounts of sludge is permissible, but the sludge should not readily form so as to require frequent cleaning of the equipment, e.g. it should not leave rings in sample bottles or tanks which require frequent cleaning. Similarly, the UAN should not foam excessively, e.g. when it is transferred into or from a tank, or when sprayed in the field as a fertilizer application, such that the foaming substantially interferes with the operation. The formation of solid precipitates is similarly undesirable, and is excessive when the precipitate interferes with processing of the UAN, e.g. settling at the bottom of tanks, plugging lines and/or equipment, and the like.

The molybdate is preferably an alkali metal molybdate such as sodium, potassium or lithium molybdate, or the like. Potassium and sodium molybdate are preferred. Sodium molybdate is especially preferred because it is readily available commercially, soluble in water and UAN, and relatively non-toxic and non-hazardous. Alkali metal molybdate has the further advantage of being a micronutrient for plants.

The molybdate is used in an amount which is effective to inhibit the corrosiveness of UAN toward ferrous metal surfaces. Generally, the use of molybdates in amounts less than 10 ppm by weight of the UAN solution are only marginally effective. While there is generally no upper limit on the theoretical amount of the molybdate which can be used, the molybdate is only soluble in trace amounts, and there is generally no benefit to be gained by using an amount in excess of 250 ppm. Sodium molybdate is preferably used in an amount which is more than 10 ppm and less than 100 ppm.

The corrosion inhibitor of the present invention is readily added to and blended with the UAN using conventional blending techniques. A tank with an agitator is all that is needed, but the molybdate can also be blended by introducing a side stream of the molybdate into the UAN and allowing sufficient mixing to be generated by turbulence as the mixture flows through piping and other equipment. The molybdate can be added as a powder or granulated solid, but is preferably an

aqueous solution, for example, from 5 to 35 percent by weight aqueous sodium molybdate. The molybdate can be added to the UAN after the urea, ammonium nitrate and any water are blended, or the molybdate can be added during the blending, or separately to the urea solution, the ammonium solution, and/or any additional water. The corrosion inhibitor can be added or blended on a batch or continuous basis.

Once the molybdate inhibitor is added to the fertilizer solution, it is effectively non-corrosive and can be stored, transported, shipped, or the like in ferrous metal equipment, such as tanks, piping, containers, application equipment or the like. In particular, the inhibited UAN can be diluted with water, generally just prior to field application as a nitrogen fertilizer for agricultural purposes. The concentrated UAN is generally diluted with at least an equal volume of water, up to 4 or 5 volumes of water. Preferably, the molybdate concentration in the concentrated UAN is sufficiently high, so that upon dilution, the diluted UAN is still effectively non-corrosive because of the presence of the molybdate. In addition, the molybdate corrosion inhibitor is also compatible with other common corrosion inhibitors for UAN such as alkyl phosphates, and with various other agricultural compositions, such as, for example, ammonium phosphate solutions, herbicide solutions, insecticide solutions, clay suspensions, herbicide suspensions, insecticide suspensions, and the like. The molybdate-treated UAN can thus be blended and/or used with common agricultural chemicals without substantial adverse consequences.

As used herein, a UAN solution is non-corrosive when the rate of corrosion of carbon steel in contact with the solution at ambient conditions is less than 250 microns per year (about 10 mils/year). The non-corrosive, dilute UAN can thus be applied to cropland for agricultural purposes, with or without dilution and/or admixture with other common agricultural chemicals, using steel or other ferrous metal equipment, such as tanks, lines, pumps, spray nozzles, and the like.

The invention is illustrated by way of the following examples.

EXAMPLES 1-5 AND COMPARATIVE EXAMPLES 1-6

The molybdate corrosion inhibition of the present invention was evaluated in a UAN solution containing 32 weight percent elemental nitrogen and 35 weight percent water. The UAN was treated with 50-200 ppm of a 35 weight percent aqueous sodium molybdate solution. For comparison, a blank was run without any corrosion inhibition, and several runs were made with an organic filmer containing nitrite, polyacrylic acid and about 2-3 weight percent molybdate (Filmer A). Corrosion was evaluated by suspending a 1020 carbon steel coupon in an open beaker of the UAN and additive, and placing the coupon and beaker in a closed oven at 31° C. for 4.75 days. The coupons were activated in 6N hydrochloric acid for 60 seconds and rinsed with deionized water to provide a clean metal surface before immersion in the UAN. At the end of the test, the coupons were removed, cleaned of any corrosion products with deionized water and paper towels, and

TABLE 1

Example	Additive	Treat Rate** (ppm)	Coupon Weight(g)		Net Loss	Corrosion Rate	
			Initial	Final		MPY	µm/year
Comp. 1	None	N/A	20.9165	20.7802	0.1363	203	5160
Comp. 2	Filmer A	50	20.8454	20.6900	0.1154	231	5870
Comp. 3	Filmer A	100	21.4076	21.2864	0.1212	180	4570
Comp. 4	Filmer A	100	21.5267	21.4230	0.1037	154	3910
Comp. 5	Filmer A	150	21.1117	21.0218	0.0899	134	3400
Comp. 6	Filmer A	200	20.8144	20.8126	0.0018	2.7	69
1	Na ₂ MoO ₄ *	50	21.5466	21.5443	0.0023	3.4	86
2	Na ₂ MoO ₄ *	100	21.3113	21.3093	0.0020	3.0	76
3	Na ₂ MoO ₄ *	100	21.4160	21.4592	0.0018	2.7	69
4	Na ₂ MoO ₄ *	150	20.4558	20.4542	0.0016	2.4	61
5	Na ₂ MoO ₄ *	200	21.3652	21.3636	0.0016	2.4	61

*35 weight percent in water.

**By weight of additive solution, including water.

dried. The weight of the coupons was measured before and after immersion in the UAN to calculate the rate of corrosion in mils per year (MPY) and microns per year. The results are presented in Table 1.

EXAMPLES 6-8 AND COMPARATIVE
EXAMPLES 7-10

The procedure of Examples 1-5 was repeated except the coupons were immersed in the UAN for 4.0 days at 31° C. in a thermostated water bath, open to the atmosphere. The results are presented in Table 2.

TABLE 2

Example	Additive	Treat Rate** (ppm)	Coupon Weight(g)		Net Loss	Corrosion Rate	
			Initial	Final		MPY	µm/year
Comp. 7	None	N/A	9.0160	8.6497	-0.3663	98.6	2500
Comp. 8	Filmer A	100	9.2293	8.9720	-0.2567	69.1	1760
Comp. 9	Filmer A	150	9.1628	8.9336	-0.2286	61.6	1560
Comp. 10	Filmer A	200	9.2337	9.0177	-0.2154	58.0	1470
6	Na ₂ MoO ₄ *	100	9.0789	9.0567	-0.0216	5.8	147
7	Na ₂ MoO ₄ *	150	9.1546	9.1387	-0.0163	4.4	112
8	Na ₂ MoO ₄ *	200	9.2603	9.2474	-0.0123	3.3	84

*35 weight percent in water.

**By weight of additive solution, including water.

EXAMPLES 9-10 AND COMPARATIVE
EXAMPLES 11-16

The procedure of Examples 1-8 was repeated except that 1010 carbon steel coupons were used, the coupons were not activated with acid but were washed with methanol and deionized water, and the test was run over in the thermostated water bath at 31° C. open to the atmosphere for a four week period. The time to initial corrosion, visibly apparent by the UAN solution turning orange, was noted for each specimen. For the purposes of comparison, other commercially available corrosion inhibitors (Filmers B and C) were also evaluated in the UAN. Also, a commercially available UAN solution believed to contain a filming inhibitor (Filmer D) at 150 ppm was also evaluated. Corrosion was calculated as follows:

$$\mu\text{m/yr} = 2159/t_{IC} \text{ (MPY} = 85/t_{IC}\text{)}$$

wherein t_{IC} is the number of days at which corrosion was visibly apparent. The results are presented in Table 3.

TABLE 3

Example	Additive	Treat Rate** (ppm)	Time to Corrosion (days)	Corrosion Rate	
				MPY	µm/year
Comp. 11	None	N/A	3	28.0	711
Comp. 12	Filmer B	150	17	5.0	127
Comp. 13	Filmer B	200	19	4.25	108
9	Na ₂ MoO ₄ *	150	>28	<3.0	<76
10	Na ₂ MoO ₄ *	200	>28	<3.0	<76
Comp. 14	Filmer C	150	3	28.0	711
Comp. 15	Filmer C	200	3	28.0	711
Comp. 16	Filmer D	150	16	5.3	135

*35 weight percent in water.

**By weight of additive solution, including water.

From the foregoing it can be seen that sodium molybdate is an effective corrosion inhibitor of steel surfaces in DAN solutions at trace concentrations. While some of the filmers (B and D) appeared to be effective as corrosion inhibitors, a film of organic material was observed floating in each of the DAN beakers for all of the filmers in Comparative Examples 2-6, 8-10 and 12-16. A relatively small amount of orange-white floe was seen early in the test in Examples 1-8, but did not increase as the test progressed. No solids formation was observed in Examples 9 and 10, suggesting that the floe in Examples 1-8 was due to the acid wash of the coupons. Separate tests corresponding to Examples 9 and 10 were allowed to stand, and after 63 days, no corrosion was observed.

EXAMPLE 11

To demonstrate the non-foaming tendencies of the molybdate, 500 ppm of the 35 weight percent aqueous sodium molybdate of Example 1 was added to the UAN of Example 1. The solution was vigorously shaken in a glass bottle. The bubbles that formed disappeared within 50 seconds after the shaking was stopped, the same result for the UAN as without the molybdate.

EXAMPLE 12

To show the compatibility of the molybdate-UAN mixture with ammonium phosphate solutions, the UAN was mixed with ammonium phosphate (18% in water) and treated with 500 ppm of the 35 weight percent aqueous sodium molybdate of Example 1. Also, a saturated solution of ammonium phosphate (about 48% in water) was treated with 500 ppm of the same sodium molybdate solution. After several days, no precipitation occurred in either of the treated solutions, and there was no indication of any deleterious reaction.

EXAMPLE 13

Ten parts by weight of the pre-emergent SURFLAN (Oryzalin) herbicide was mixed with 90 parts by weight of the UAN of the previous examples (without dilution), with and without 500 ppm of the 35 percent aqueous sodium molybdate solution. Upon vigorous shaking, a small amount of foaming occurred in each bottle and a semi-stable orange suspension formed. The orange powder precipitated out over a 24-hour period. The stability of the foam and suspension was not altered by the molybdate.

EXAMPLE 14

Ten parts of ROUNDUP herbicide solution was mixed with 90 parts of the UAN, with and without the molybdate as in Example 13. Both mixtures formed a homogeneous solution with no foam, and there was no difference observed with the presence of the molybdate.

EXAMPLES 15 AND 16

The procedure of Example 13 was repeated using DIAZINON insecticide solution, and then DURSBA insecticide solution, with and without molybdate treatment. These mixtures formed emulsions along with a small amount of foam. The DURSBA insecticide/UAN emulsion began to break after about 5 minutes, but the DIAZINON insecticide/UAN emulsion lasted about 15 minutes. In either case, the sodium molybdate had no impact on foaming or the stability of the emulsion.

EXAMPLES 17 AND 18

The procedure of Example 13 was used to mix 10 parts of a slurry of bentonite clay in water and methanol with 90 parts of the UAN solution, with and without 500 ppm of the 35 weight percent sodium molybdate solution. A stable suspension without foaming was obtained. The molybdate had no observable effect. The tests were repeated with an additional 2 weight percent of powdered BARRICADE 65 WG herbicide. Relatively stable yellow suspensions without foaming were obtained, and again the molybdate had no observable effect.

The foregoing results of Examples 11-18 demonstrate that the sodium molybdate corrosion inhibitor, even at a relatively high treatment rate (175 ppm), has no observable effect on the physical properties of solutions or mixtures of UAN with various common agricultural chemicals.

The foregoing description of the invention is illustrative and explanatory thereof. Various changes in the materials, apparatus, and particular parts employed will occur to those skilled in the art. It is intended that all such variations within the scope and spirit of the appended claims be embraced thereby.

We claim:

1. In a method for inhibiting corrosion of ferrous metal surfaces by nitrogen fertilizer solutions in contact

therewith, including the steps of blending a corrosion inhibitor with a fertilizer solution consisting essentially of urea, ammonium nitrate and a minor amount of water, and contacting the metal surfaces with the resulting blend, the improvement consisting of:

5 using an effective, soluble amount less than 200 ppm, by weight of the fertilizer solution, of an alkali metal molybdate as the corrosion inhibitor in the blending step.

2. The improvement of claim 1, wherein the amount of molybdate used is more than 10 ppm and less than 100 ppm by weight of the fertilizer solution.

3. The improvement of claim 1, wherein the fertilizer solution contains from about 20 to about 50 percent by weight water and has a pH from about 7 to about 8.

4. The improvement of claim 1, wherein the fertilizer/molybdate blend is essentially free of sludge-forming compounds, of excessive foaming characteristics and of precipitates.

5. The improvement of claim 1, wherein the alkali metal molybdate is added to the fertilizer solution as an aqueous solution comprising at least 65 weight percent water.

6. The improvement of claim 1, wherein the molybdate comprises sodium or potassium molybdate.

7. A method for processing a liquid nitrogen fertilizer in ferrous metal equipment without excessive corrosion, consisting of the steps of:

(a) blending (1) a solution of urea, (2) a solution of ammonium nitrate, (3) optional water and (4) an aqueous solution of an alkali metal molybdate;

(b) recovering the blend from step (a), wherein the blend is effectively inhibited against ferrous metal corrosion and comprises a precipitate-free, non-sludging, non-foaming solution containing more than 10 and less than 100 ppm of the alkali metal molybdate and from about 20 to about 50 percent water;

(c) passing the corrosion-inhibited blend in contact with ferrous metal surfaces.

8. The method of claim 7, comprising adjusting the pH of the blend to between 7 and 8 with ammonia.

9. The method of claim 7, wherein the aqueous molybdate solution comprises from about 5 to about 35 weight percent sodium or potassium molybdate.

10. The method of claim 7, comprising storing or transporting the inhibited fertilizer solution in ferrous metal piping or containers, then diluting the inhibited fertilizer solution with at least an equal volume of water, wherein the diluted fertilizer solution is effectively inhibited against corrosion of ferrous metal surfaces, and then applying the diluted fertilizer solution to cropland with ferrous metal equipment.

11. The method of claim 7, comprising storing or transporting the inhibited fertilizer solution in ferrous metal piping or containers, then mixing the fertilizer solution with another agricultural chemical selected from the group consisting of ammonium phosphate, herbicide and insecticide solutions, and clay, herbicide and insecticide suspensions, wherein the physical properties of the fertilizer/agricultural chemical mixture are substantially unaffected by the molybdate, and making an agricultural application of the mixture.

12. A corrosion-inhibited liquid fertilizer, consisting of a non-sludging, non-foaming, precipitate-free solution of urea and ammonium nitrate, of more than 20 and less than 50 percent water by weight and from 10 to 100 ppm sodium or potassium molybdate, having a pH of from 7.5 to 8.0 at atmospheric pressure and essentially non-corrosive to ferrous metal surfaces.

* * * * *