FERTILIZER ADDITIVES AND SOIL CONDITIONERS

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents, issued since January 1965, that deal with fertilizer additives and soil conditioners.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of fertilizer additives and soil conditioners.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The large Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

15 Reasons Why the U.S. Patent Office Literature Is Important to You –

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.

2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.

5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.

6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.

7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.

8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.

9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.

10. Obtain licenses — many U.S. chemical patents have not been developed commercially.

11. Patents provide an excellent starting point for the next investigator.

12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.

13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.

14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.

15. It is a creative source of ideas for those with imagination.

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INTRODUCTION

Agricultural science represents perhaps one of the oldest sciences known and practiced by man. Broadly speaking, this may include all the efforts by man, both past and present, to improve the efficiency of the growing cycle, production, quantity, food value, size, etc., of a given living plant.

Worldwide governmental and social attention is increasingly focused on the food supply balance and the needs for improving yields to feed a rapidly growing world population. This problem is particularly severe in the developing and underdeveloped nations as they strive to achieve a modern social and industrial structure while becoming self-sufficient in the agricultural sector. High volumes of the basic macronutrients, nitrogen, phosphorus and potassium are now being produced and formulated in almost every country.

In recent years, agricultural product development has been directed to a large variety of additive or complimentary products to improve fertilizer production, application and efficiency to fit the needs of modern agricultural practice while reducing the unit cost of production.

In the processing of fertilizers, many additives have been developed to improve product handling for both liquid and granular products as well as providing controlled release of nutrient values and improved soil conditioning.

The development of good soil structure with its beneficial effects on drainage, aeration, rooting and nutrient uptake is important to the production of agricultural crops. A synthetic chemical which will improve soil structure is valuable for increasing yields in presently cultivated areas and for expanding production into previously structurally inhibiting soils. Additional benefit is derived from such a chemical if, on degradation in the soil, an essential nutrient such as nitrogen is released.

It is known that plants require various mineral elements in their diet before they can synthesize the organic constituents needed to stimulate their growth and development. These elements fall into three classifications—primary or major, secondary, and minor or trace elements.

The primary or major elements, also known as macronutrients, include nitrogen, phosphorus, and potassium. The secondary elements include calcium and sulfur. The minor or trace elements, commonly referred to as micronutrients, include the metals zinc, manganese, copper, iron and magnesium.

The primary and secondary elements are generally applied to the soil in which plants are grown in large amounts in the form of highly refined and concentrated raw fertilizer materials. While the use of these highly refined materials is desirable, they do present a problem since, due to their refined nature, most of the trace metals normally present as impurities are no longer part of the fertilizer. In addition, the high crop production per acre resulting from the use of the refined fertilizers rapidly depletes the amount of trace metals available in the soil.

It is, therefore, widely recognized that the addition of trace metals, or micronutrients, to the soil is essential to increase crop production and yield. The specific effect of the micronutrients on the growing crop is not known; however, it has been theorized that the micronutrients act in a catalytic manner in promoting the organic reactions taking place in the plants thereby advancing the maturity of crops and increasing seed production.

Since the micronutrients are required in only small amounts it is difficult to get proper distribution of these elements in the soil. Simple inorganic materials, such as the sulfates and oxides of the trace materials, were originally used as the carriers for the micronutrients. The micronutrients have also been combined with organic compounds in the form of complexes or chelates. These organic micronutrient complexes or chelates are thought to be more readily available to the plant and, therefore, more effective than the inorganic micronutrient compounds. Micronutrients have also been applied to the soil in the form of glass frits containing the micronutrient. These are prepared by adding micronutrients to molten glass and grinding the glass after it has hardened.

Micronutrient elements are now being used as a tool in maintaining the productivity of our agricultural soils and in increasing the yield and quality of crops grown on them. In many cases micronutrients are not only being used to correct known deficiencies but they are also being used in programs for the maintenance of soil fertility.

This book describes over 190 processes related to the improvement of fertilizer compositions and soil conditioners. These processes, described in the patent literature of the United States illustrate the research and development effort that is being continually pursued to meet the universal needs of mankind. Processes developed in over twelve countries are described in this book.

ADDITIVES AND PROCESSING AIDS FOR GRANULAR PRODUCTS

GRANULATION AIDS AND PROCESSES

Tetrapotassium Pyrophosphate

U. Hauschild; U.S. Patent 4,008,065; February 15, 1977; assigned to Kali-Chemie AG, Germany describes a fertilizer composition containing an improved and more effective granulating adjuvant. The process provides a granulated fertilizer composition comprising mineral phosphates calcined with alkali and between 0.5 and 15%, preferably 1 and 10%, by weight of tetrapotassium pyrophosphate $K_4P_2O_7$. The granulated fertilizer composition, preferably having a particle size between 0.5 and 3 mm, may also contain other plant nutritive agents of conventional type, for example, potassium salts, magnesium salts, and/or nitrogen compounds, as well as one or more other conventional fertilizer granulating adjuvants and/or binding agents.

The process comprises the steps of mixing together ground alkali-containing calcined phosphate and between 0.5 and 15%, preferably between 1 and 10%, by weight of tetrapotassium pyrophosphate $K_4P_2O_7$, granulating the resulting mixture with water, typically between 7 and 15% thereof, and drying the resulting granules, typically at a temperature between 105° and 200°C.

In carrying out the process, preferably at least 85% of the ground calcined phosphate has a particle size smaller than 0.15 mm and comprises compounds having a molar ratio of P_2O_5:Me_2O:CaO = 1:0.9 to 1.6:3.0 to 4.1 (Me_2O = Na_2O or K_2O); or of P_2O_5:Na_2O:CaO = 1:0.2 to 1.1:2.0 to 3.1. Also, the calcined phosphate may contain one or more additional known plant nutritive agents, and/or one or more other conventional fertilizer granulating adjuvants during the mixing step.

Example 1: 1,000 parts of ground alkali-containing calcined phosphate (Rhenaniaphat having 29.2% P_2O_5, 17.6% Na_2O, 38.6% CaO and a P_2O_5 solubility in Petermann solution of 98.1%) is mixed with 80 parts of tetrapotassium pyrophosphate, and the admixture is mixed in a rotating mixer-granulator with water (approximately 11%) for a period of time sufficient to form moist granules. The "green" granules which fall predominantly in the range between 0.5 and 2.5 mm, are next dried up to a temperature of 160°C in a drying drum which is directly heated with gases. After cooling, the mechanical and analytical investigations are performed. The results are summarized in the following table:

	Example 1	Without $K_4P_2O_7$ Addition
Yield in granule size range of 0.5-2.5 mm.	90.2%	32%.
Total yield after breaking and sieving of oversize granules	92%	35%
Average breaking limit of 50 granules	1.39 kp	0.25 kp
Abrasion after 10 falls from 10 m. height, <0.5 mm.	2.4%	14%
Decomposition of the granules in water after 2 minutes	100%	10%
Total P_2O_5 content	30.2%	29.1%
P_2O_5 solubility in Petermann-solution	99.2%	96.7%
P_2O_5 solubility in Water	11.4%	0.9%
K_2O content	4.3%	0.1%

The product flows freely and develops practically no dust.

Examples 2 and 3: Two different mixtures of the alkali-containing calcined phosphate utilized in Example 1 and potash salt (comprising predominantly potassium chloride) are mixed with the amounts of $K_4P_2O_7$ specified below, and the mixtures are granulated with water in the identical fashion as in Example 1. Subsequently, the granules are dried and cooled in a manner analogous to Example 1. The essential data and analysis results are set forth in the following table:

Example No.	2		3	
Mixture	Content of P_2O_5=17.8% K_2O = 19.2%		Content of P_2O_5=14.8% K_2O = 24.6%	
$K_4P_2O_7$ Addition	3.1%	None	2.7%	None
Granules, dry granule size 0.5-2.5 mm.	81%	34%	82%	33%
Breaking limit	1.13 kp	0.31 kp	0.89 kp	0.28 kp
Abrasion	3.6%	18%	3.6%	22%
Decomposition in water	100%	80%	100%	85%
Total P_2O_5	18.5%	17.8%	15.5%	14.8%
Petermann-solubility	99.1%	97.9%	99.1%	97.8%
P_2O_5 Water solubility	7.7%	0.9%	8.1%	0.9%
K_2O Content	20.6%	19.2%	25.2%	24.6%

Mixtures with only 0.5% $K_4P_2O_7$ addition still lead to clearly better results than in the case of no $K_4P_2O_7$ addition. The granulated material obtained with the addition of $K_4P_2O_7$ permits easy handling, is well adapted for storage and develops practically no dust.

Humic Material

S. Nagasawa, T. Nakano and K. Sakashita; U.S. Patent 3,617,237; November 2, 1971; assigned to Mitsui Toatsu Chemicals, Inc., Japan describe a process for producing granular compound fertilizers which comprises mixing humic substance obtained from peat (such as grass peat and forest peat) with a mixture of the starting fertilizer materials and granulating by tumbling, kneading or extruding the thus-obtained mixture to form a granular compound fertilizer. The humic substance is obtained by disintegrating peat in water to suspend the humic substance and the fibrous substance in the water and separating the humic substance from the suspension.

The humic substance is preferably added to the fertilizer materials prior to granulation and is added in an amount of at least 1 dry weight percent, preferably at least 3 dry weight percent, especially 3 to 30 dry weight percent, based on the dry weight of the total resulting mixture including the humic substance and fertilizer materials. In the example all parts and percentages are by weight.

Example: A high quality peat (having a weight ratio of fibrous substance to humic substance of 6:4) collected in the Sarobetsu plain in Hokkaido, Japan, was beaten in water to form a suspension containing the fibrous substance and humic substance. The fibrous substance was separated from the suspension with a 20-mesh screen. The remaining suspension containing humic substance was centrifuged to separate the solid humic substance. The humic substance thus obtained was dried to a water content of 50% and was sieved with a 1,000-μ sieve and all that part of it passing through the sieve was recovered and used as an additive. The same high quality peat was dried as it was to a water content of 50% and was crushed and all that part passing through the 1,000-μ sieve was recovered and used as an additive for comparison.

Amounts of 30 to 500 parts of each of the abovementioned additives were added to the total of 817 parts of a mixture containing 133 parts of urea, 172 parts of ammonium sulfate, 233 parts of monoammonium phosphate, 43 parts of calcium superphosphate, 209 parts of potassium chloride and 27 parts of magnesium hydroxide. A total of 1 kg of the mixed raw materials was put into a pan granulator having a diameter of 45 cm and a mixing rate of 32 rpm, and was rotated for 10 minutes while spraying water to granulate the materials. The granulation ratio was determined by measuring the weight percentage of granules having a grain size falling in the range of 1.3 to 3.5 mm.

In addition, the process was repeated but instead of sieving the granular material after granulation, it was fed, together with heated air at an inlet temperature of 250°C, into a cylindrical rotary drum dryer having a diameter of 30 cm and a length of 1 m and rotating at 15 rpm. The amount of fertilizer material adhering on the dryer wall was measured and its state was observed.

For comparison, peat and the aforementioned fibrous substance separated from the suspension containing humic and fibrous substances were also tested separately. The advantages of the process and the results of the comparisons are shown in the following table. Each of the additives contained 50% by weight of water. The adhesion ratio is the weight percentage of fertilizer materials which adhere to the dryer wall based on the total weight of fertilizer materials fed through the dryer.

The following advantages are obtained according to the process: First, the granulation ratio of the compound fertilizer is increased and the adhesion of granules to the dryer wall in the drying step is substantially reduced. Second, the granular compound fertilizer obtained by the process is very high in storability and does not coagulate even when it is stored for long periods of time. Third, sterilization of soil is prevented by applying the compound fertilizer which contains the humic substance and an acceleration of the growth of crops and increase in the fertilizing effect by the combination of the fertilizer and humic substance is observed.

Additive			Results of Granulation Test		Results of Dryer Adhesion Test	
	Parts	Percent*	Granulation Ratio (%)	Ease of Granulation	Adhesion Ratio (%)	Adhesion of Granules to the Dryer Wall
Comparison						
Peat	80	(4.67)	32.5	2	12.6	2
Peat	300	(15.5)	27.6	2	8.3	3
Process						
Humic substance	30	(1.8)	38.1	4	3.8	4
Humic substance	80	(4.67)	54.3	5	1.5	4
Humic substance	150	(8.4)	66.9	5	1.2	4
Humic substance	300	(15.5)	72.5	5	1.3	4
Humic substance	500	(23.4)	71.8	5	1.2	4
Comparison						
Fibrous substance	80	(4.67)	27.6	2	17.8	2
Fibrous substance	300	(15.5)	18.8	1	16.5	2
No additive	—	0	33.4	3	17.1	1

*Percentages in parenthesis are percentages of additives in the total mixture of fertilizer materials and additive on a dry basis.

Granulation Test:

(1) Substantially not granulated.
(2) Small granules were so many that it was difficult to granulate the mixture.
(3) Granules tended to become too large.
(4) Rather easy to granulate the mixture.
(5) Grain size was so uniform that it was easy to granulate the mixture.

Dryer Adhesion Test:

(1) Considerable adhesion 40 cm from inlet.
(2) Rather little adhesion.
(3) Little adhesion.
(4) Substantially no adhesion.

Wetting Agent

J.M. Petkovsek and C.O. Rodriguez; U.S. Patent 3,620,709; November 16, 1971; assigned to International Minerals & Chemical Corporation have found that superior potassium sulfate granules may be obtained by wetting finely divided potassium sulfate with an aqueous solution containing potassium sulfate, magnesium sulfate and starch, granulating the wetted potassium sulfate particles and drying the granulated particles.

The process provides granules having the desired stability and maintains reduction of product grade to a minimum. The potassium sulfate component of the binder solution obviously does not reduce product grade. Indeed, the potassium sulfate of the binder becomes part of the product that is useful to the purchaser and is calculated in the sale price of the fertilizer since it represents K_2O values. While the magnesium sulfate does reduce the product grade slightly, the sulfate moiety of the magnesium salt is common with the sulfate of the potassium sulfate.

Potassium sulfate produced by the metathetical reaction between potassium chloride and langbeinite may produce potassium sulfate fines having a grade as low as 50.5% K_2O. Inasmuch as commercial specifications require 50% K_2O products, it is apparent that, in these instances, the binder must be selected to avoid any substantial product grade reduction.

It appears that the magnesium sulfate and potassium sulfate of the binder solution in some manner form a complex salt that significantly enhances the strength of the granules. Neither magnesium sulfate alone nor potassium sulfate alone provides granulated products comparable to those provided when the binder solution contains both magnesium sulfate and potassium sulfate. In a preferred case the aqueous solution will contain from 2.5 to 6% magnesium sulfate, from 2 to 12% potassium sulfate, and from 2.5 to 3.5% starch.

Example 1: Potassium sulfate granules of –20 mesh ranging down to fines were wetted with the binder solutions indicated below by spraying the particles with the solution while the particles were being tumbled in a drum granulator. The solution was applied to provide a moisture content of 10% as water. After granulation the particles were dried in a 14" x 8' rotary drier operating at 7 rpm. The product was discharged at a temperature of 150°C and a moisture content of just below 1%.

Table 1 demonstrates the effect of varying proportions of binder solution on the degradation of the product in the drier. A test with starch demonstrates that starch alone is not an effective binder. Potato starch was employed in runs 1 through 4 and 7 of the table, while pearl corn starch was employed in runs 5 and 6.

Product degradation was determined by placing 500 g of a very narrow size fraction of product, generally –8+10 mesh, in a jar mill together with two steel bars ½ inch in diameter and 5½ inches long. The mill was operated for 5 minutes and percent degradation is the percent by weight of material which falls outside the specified narrow range, i.e., which will pass a 10-mesh sieve.

TABLE 1

Run	. . . . . Binder, % by weight			Product Degradation
No.	$MgSO_4$	K_2SO_4	Starch	(%)
1	13	9.3	2	21
2	13	9.3	1	20
3	7.3	5.3	2	33
4	7.3	5.3	1	31
5	13	9.3	2	16
6	13	9.3	1	21
7	–	–	2	51

Example 2: Example 1 was repeated using the binder solutions and conditions set forth in Table 2. Drier operation was in countercurrent direction. Gelatinized corn starch was employed. The screen size analysis of the feed and drier discharge were as shown.