

ALIEN PROPERTY CUSTODIAN

SOIL IMPROVERS

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It has been proposed to manufacture soil improvers by maintaining materials containing a substantial amount of humin acids, hydrated silicic acid and hydrated alumina in a moist condition at elevated temperature for a period of time sufficient to produce colloidal complex compounds of humin acids, silicic acid and alumina. These complex compounds are capable of producing compounds with bivalent bases with a high interchanging power for bases, which have a very beneficial action on the soil.

I have now found that certain compounds of humin acids with alumina, preferably not less than 1%, calculated as Al_2O_3 on the dry organic matter present in the material, are very active soil improvers, especially for soils containing a substantial proportion of clay. The dispersibility of the said compounds can be increased by incorporating monovalent bases, such as sodium, potassium or ammonium.

If desired calcium and/or magnesium may also be incorporated to a certain degree, which has the effect that for instance the manufacturing process is improved as the complex compounds containing calcium and/or magnesium are easier to separate from the aqueous suspension by filtration processes.

Experiments have shown that complex compounds of the character indicated above are of great value for improving the properties of the soil. They have a favourable influence on the crumb structure and increase the active surface of the soil, owing to the fact that the size of the crumbs of the soil is materially reduced. They also increase the specific volume of the soil and have a favourable influence on the ratio of air, water and solid material within the soil. They have a retarding influence on the evaporation of the water from the soil, by promoting the formation of a dry thin layer at the surface, which prevents rapid evaporation of water from the interior.

Moreover the crumb structure in a soil, treated with a soil improver according to the invention, is more resistant against water so that the porosity of the soil, especially after heavy rains, is better maintained.

It is known in the art to produce materials rich in humin acids by subjecting fossil or recent organic materials, such as sphagnum peat, to an oxidizing process. Materials of this character also show the above mentioned favourable action on the soil to a certain extent; however, by incorporating aluminium in the said materials the soil improving properties are highly increased, so

that the same effect on the soil is obtained with a considerably lower addition than in the case of aluminium free humin materials. The amount of the soil improver according to the invention required to effect the desired improvement is therefore very small which is of great economical importance.

The aluminium can be completely or partly replaced by iron.

If potassium or ammonium are used as monovalent bases the soil improvers also act as fertilizers.

The soil improvers according to the invention generally do not contain silicic acid, as the presence of silicic acid in the complex compounds has an unfavourable influence on the action of the same in soils containing clay. However, I also wish to claim products containing a certain amount of silicic acid as far as they are not covered by the patent No. ——— (application No. 717,536).

The soil improvers according to the invention are manufactured by causing products rich in humin acids to react in the presence of water with aluminium and/or iron compounds under such conditions that both the humin acids and the aluminium or iron compounds are in dissolved or finely dispersed state, preferably at an elevated temperature, so as to produce complex compounds of humin acids and alumina.

In order to explain the process which is the object of the invention I shall describe the reactions which will occur when humin acids are made to react with aluminium compounds according to the invention.

The humin acids may be produced e. g. by subjecting sphagnum peat to an oxidizing process by blowing air through the material heated to a temperature of $120^{\circ}C$ under a pressure of 10 atmospheres and periodically or continuously introducing ammonia in gaseous or liquid form so as to maintain the pH value between 6 and 7. A process of this character has been described in Patent No. ——— (Application No. 717,536). The humin acids are now separated from the oxidized material by extracting the same with aqueous ammonia, acidifying the solution and washing the precipitate.

The humin acids obtained in this way are dispersed in water and ammonia is gradually added so as to produce a dispersion having a pH of 7. To this dispersion I slowly add a solution of aluminium sulphate, preferably at a moderately elevated temperature, the amount of aluminium sulphate added being about $2\frac{1}{2}\%$, calculated as

Al₂O₃ on the dry organic material. By this addition the pH is lowered from 7 to about 5 and the liquid becomes gelatinous.

When I now add sulphuric acid until the pH is decreased until about 4.3 a complex compound of humin acid and aluminium hydrate is produced in flocculated form. This complex compound can be separated from the liquid by filtering and I have found that it holds the aluminium so firmly bound that it can only be dissolved out by washing the substance with strongly acid solutions having a pH lower than 2 or with strongly alkaline solutions.

If during the reaction of the humin acids with aluminium sulphate the pH is allowed to decrease below 4, e. g. by adding a larger amount of aluminium sulphate, e. g. 5%, calculated as Al₂O₃, the mixture has a too strongly acid reaction to maintain the humin acids in finely dispersed condition and in the resulting products the aluminium will not be firmly bound. This is proved by the fact that a great part of the aluminium will already be dissolved when extracting the solid material with weakly acid solutions, e. g. solutions having a pH of 2½-4.

On the other hand complex compounds containing the aluminium in firmly bound condition will be obtained when after adding e. g. 2½% alumina in the form of aluminium sulphate the pH value is increased until about 7 by adding ammonia and then the remaining 2½% of the aluminium sulphate is added.

I shall now describe the process of manufacturing soil improvers according to the invention as it is carried out for technical purposes.

The aluminium compound is generally added in the form of a soluble salt, e. g. aluminium sulphate or aluminium chloride. I may also use aluminium hydrate in a finely dispersed form; e. g. in gel form; however in this case it is not possible to carry out the reaction at elevated temperature as the aluminium hydrate has the tendency to flocculate and to lose the high degree of dispersion necessary for the present purpose when heated.

A suitable starting material for practical purposes is a solution of aluminium ores e. g. of bauxite or clay, in sulphuric acid.

The humin acids are generally not used in isolated condition, but in the form of the material obtained by subjecting certain organic materials to an oxidizing process.

According to an embodiment of the invention the humin acids are produced, either before, during or after the addition of the aluminium compounds, by subjecting fossil or recent organic materials to an oxidizing process by blowing air through the material in moist condition at a temperature not substantially exceeding 130° C. The proportion of humin acids produced can be increased by maintaining the pH value during oxidation below 9, preferably between 6 and 7. This regulation of the pH has a very favourable influence on the oxidation and polymerisation processes of the substances present in the peat so that humin acids of the desired properties are obtained.

The pH is controlled by periodically or continuously introducing alkaline substances, such as ammonia in gaseous or in dissolved form. This treatment should preferably be continued until the absorption of oxygen by the material is practically finished, as the products obtained in this way have proved to be very resistant against bacterial oxidation in the soil.

A suitable starting material for producing humin acids by the aforementioned oxidizing process is sphagnum peat and the invention will be illustrated by examples in which sphagnum peat is used. However, other recent or fossil organic substances are also suitable, e. g. straw, paddy straw, refuse of sugar factories (bagasse and pulp), lignite and charcoal.

The material rich in humin acids which is produced by the processes described above is so treated as to bring the humin acids into finely dispersed condition. This is effected by increasing the pH to about 7, preferably by adding ammonia and heating the mixture to a temperature of e. g. 60° C. The mixture may have the form of an aqueous suspension and in this case it will contain e. g. 5 parts by weight of water on 1 part by weight of dry organic substance; however, it may also be a solid, relatively dry mass which contains e. g. 2 parts by weight of water on 1 part by weight of dry organic substance. Preferably the consistency of the reaction mixture should be such that it can be easily stirred.

The material containing the humin acids in finely dispersed condition is now made to react with the aluminium salt solution, e. g. an aluminium sulphate solution and, as pointed out above, care should be taken that the pH value of the reaction mixture remains within the range of pH values necessary for maintaining the humin acids in finely dispersed condition. The pH generally should not decrease below a value of about 4.8.

According to an embodiment of the invention the pH value of the reaction mixture is maintained between 4 and 8 by alternately adding an aluminium salt solution and an alkaline substance, preferably ammonia. By way of example I may mention that by adding 2½% of alumina in the form of aluminium sulphate the pH is generally lowered to about 5. By adding ammonia I increase the pH to about 7 with the result that the colloidal substances are finely dispersed again. I can now add a further quantity of aluminium sulphate solution, e. g. corresponding to 2½% of alumina, without risking the pH value to be lowered substantially below 5.

When the desired complex compound has been definitely formed, the aluminium is firmly bound and the pH may now be lowered as far as 2 without the danger of dissolving out part of the aluminium. However for obtaining a product which can be easily separated from the aqueous liquid by filtration it is sufficient to adjust the pH to a value of about 4½-5.

After filtration the pH value of the final product is advantageously adjusted between 6 and 8, preferably at about 7 so as to obtain a soil improver which can be easily dispersed in water.

The oxidizing process of the organic starting materials can be effected before, during or after the treatment with the aluminium compound, but it is preferred to carry out the oxidizing process first and then to add the aluminium compound.

The binding of the aluminium in the complex compound and the colloidal properties in general of the oxidized and polymerized product may be improved by treating the organic material before the oxidizing process with water, preferably acid or alkaline and preferably at elevated temperature.

When using an acid or alkaline liquid for this treatment the mixture, if desired, may be washed with water before subjecting the same to the oxidizing process. The treatment with water or

dilute acid or alkali can also be effected after the oxidizing process but before the addition of the aluminium compound. In this case too the treatment is preferably effected at elevated temperature and the mixture may be washed with water before adding the aluminium compound. A distinct improvement is e. g. already obtained by heating the reaction mixture after the oxidizing process with water, whereas the same treatment before the oxidizing process gives less satisfactory results. It is not improbable that the organic material or the oxidized and polymerized organic material contains derivatives of reducible sugars which enter into the complex aluminium compounds and have an unfavourable influence on the binding of the aluminium in the same, so that it can be expected that a treatment of the organic material which tends to remove the said sugar derivatives or to convert the same into harmless or even useful substances will improve the properties of the final product.

According to a further embodiment of the invention calcium and/or magnesium are incorporated into the complex aluminium compounds by adding calcium and/or magnesium compounds before, during or after the reaction between the material rich in humin acids and the aluminium compound. A product containing calcium can be obtained e. g. by neutralizing the product obtained by the reaction with aluminium sulphate partly with calcium hydrate and partly with ammonia.

The soil improvers obtained according to the invention can be easily dispersed in the soil. They have a favourable influence on the crumb structure and improve the aeration of the soil and retard the evaporation of the water from the same. The remarkable influence of the complex aluminium compounds according to the invention on the size of the crumbs can be shown by the following test:

Finely pulverized clay is mixed in a suitable vessel provided with a stirring device with 15-35% of water, dependent from the material used. Owing to the plastic condition of the clay particles aggregates are formed which can be compared with the crumbs in the soil and which under predetermined conditions attain a certain size. I have now found that by adding a small amount of the soil improver according to the invention the size of the crumbs is materially reduced.

The amount of the complex aluminium compound required is very small. In several tests I have found that an addition to the clay of e. g. 0.1% of the technical soil improved (corresponding with about 0.07% of dry organic matter) is sufficient to obtain the optimum value for the reduction of the size of the crumbs. However this value is only mentioned by way of example as it will obviously be dependent from the character of the soil to be improved and the soil improver used.

The invention will be further explained by the following examples:

Example 1

In an autoclave provided with a suitable stirring device 1½ kilograms of sphagnum peat (containing about 20% of water) and 0.9 litres of water are heated at a temperature of 125-130° C and a pressure of 10 atmospheres. Air and ammonia are introduced into the autoclave.

The amount of air is about 400 litres per hour and the amount of ammonia is controlled so as to

maintain the mixture substantially neutral or slightly acid (pH5-7, 6-7). This can be attained by gradually reducing the amount of ammonia introduced during the reaction which takes about 8 hours. In the beginning gaseous ammonia is introduced in an amount of 75 litres per hour and I finish with small amounts of ammonia, which are preferably added in the form of a solution by means of a sluice device.

The product obtained in this way is mixed with a suitable amount of water so as to obtain a mixture which can be easily stirred. It is adjusted at a pH of about 7. I then slowly add a dilute aluminium sulphate solution, the mixture being continuously stirred and maintained at a temperature of 60° C or higher. This step can also be carried out in the autoclave.

The total amount of aluminium salt added to the mixture is about 5%, calculated as Al₂O₃ on the dry organic material.

The addition of aluminium sulphate is preferably carried out in stages, by first adding aluminium sulphate until the pH value has been lowered to about 5; this is the case when one half of the aluminium sulphate has been added. I now increase the pH value again till about 7 by introducing ammonia and I then slowly add the other half of the aluminium sulphate solution with stirring. The final pH value is 4.5-5. Calciumhydrate can be added if desired in this stage.

The reaction mixture is left to stand for some time. The soil improver settles down from the solution and is separated from the supernatant clear liquid. If desired the product can be made slightly more acid. It can be dewatered in a filter press or a continuous filter, and subsequently can be dried.

The product obtained has a too strongly acid reaction to be readily dispersible and it is therefore brought at a pH of 7 by adding ammonia. If a product containing calcium is desired neutralisation is effected partly with ammonia and partly with calciumhydrate, one third of the free equivalents being saturated by calcium and two thirds by ammonia.

The product is easily dispersed in the soil where it improves the crumb structure and in connection therewith the aeration. It also has a favourable influence on the behaviour of the water in the soil.

Example 2

The process is carried out in the same way as in example 1, but after the oxidizing process the reaction mixture is boiled with water for about 2 hours. It is then converted into the complex aluminium compound after the method described in example 1.

Example 3

This example refers to a process in which the incorporation of the aluminium compound and the production of humin acids are carried out simultaneously. The oxidation process corresponds to that of example 1 with the following difference:

The sphagnum peat is boiled for six hours with a solution of 2.5% HCl, filtered and washed. The aluminium sulphate solution is slowly added by means of a sluice device. The addition of this solution is started after an oxidation period of two hours, according to example 1. Half of the aluminium solution is added in about 15 minutes. During the whole process the mass is energetically stirred so that a thorough mixture is ob-

tained. After the addition of the aluminium sulphate ammonia is added until the mixture (which has been rendered acid by the aluminium sulphate) is practically neutral.

I then continue the oxidizing process. After the third hour I again add aluminium sulphate and neutralise again with ammonia. The oxidation process is further carried through as described in example 1.

The total amount of aluminium sulphate added in this example may, for instance, amount to about 2.5 parts by weight of Al_2O_3 on 100 parts by weight of dry organic material.

Example 4

In this example the starting material for the oxidizing process consists of sphagnum peat treated with dilute acid at elevated temperature, so as to invert and to remove the reducible sugars. The sphagnum peat ordinarily used yields about 13-18% of reducible sugars. Removal of the sugars is effected by boiling the peat with dilute hydrochloric acid (2½%):

1000 grams of sphagnum peat treated as described above and still containing 1,9% of reducible sugars are mixed in an autoclave with 667 grams of water. The autoclave is heated to a temperature of 120° C and 340 litres of air per hour are blown through the reaction mixture. The pH is maintained between 6 and 7 by introducing ammonia (30%) by means of a sluice device.

The product is then adjusted at a pH of 7. Water is added in an amount of 2 parts by weight on 1 part by weight of dry organic material. A

dilute solution of aluminium sulphate is now slowly added in an amount corresponding with 2.5% of Al_2O_3 , calculated on dry organic matter.

The final product is adjusted at a pH value of 7.

Example 5

The oxidizing process is effected in the same way as in example 1.

After the oxidizing process the product is washed with hydrochloric acid (2½%) and filtered. In the beginning the filtrate is coloured. The washing is continued until the filtrate is practically colourless. The product is treated thereafter as in example 1 as concerns the addition of aluminium.

Example 6

The oxidizing process is effected in the same way as in example 1. The oxidized product is mixed in the autoclave with water so as to obtain a suspension containing 4 parts by weight of water on 1 part by weight of dry organic matter.

Ammonia is added so as to increase the pH to 9 and the product is then heated at 120-130° C during six hours.

The product obtained in this way is treated with an aluminium sulphate solution according to the processes described in one of the preceding examples and the complex compounds obtained thereby contain the aluminium in firmly bound condition.

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