Granular fertilizer with controlled release of nutrients can be prepared by coating the fertilizer with a mixture consisting of the alkyl resin containing cross-linkable functional groups with mean molecular weight between 500 and 2000 in the amount 30 to 80 % w/w, amino resin in the amount of 1 to 30 % and vegetable oil in the amount of 30 % w/w. The coating mixture contains 66.6 % w/w of alkyl resin, 16.8 % w/w of amino resin, 8.3 % w/w of castor oil and 8.3 % w/w of butylalcohol, and the fertilizer is coated by gradual spraying of 3 to 20 doses of the coating mixture, wherein the coating is performed in the rotary cylindrical container or fluid apparatus at the temperature of 60 to 120 °C. The layer of coating mixture makes 6 to 25 % w/w of the overall weight of the coated granule.
GRANULAR FERTILIZER WITH CONTROLLED RELEASE OF NUTRIENTS

Field of the Invention

The invention relates to a granular fertilizer with controlled release of nutrients, which can be prepared by coating the granules of fertilizer with a mixture of alkyd resin, amino resin and vegetable oil. The release rate is regulated by the amount and ratio of alkyd resin to amino resin.

Background of the Invention

Nutrition of plants depends on the accessibility of mineral nitrogen, phosphor and potassium in soil. A wide range of mineral fertilizers is produced throughout the world, differing only in mutual ratio of these three components, or also by the presence of other elements (Mg, S, Ca) or trace elements. All these mineral fertilizers have a high solubility in water, which is their common disadvantage. This problem can be solved essentially by developing new types of fertilizers, which provide for a slower release of nutrients into soil, so that they are utilised gradually. Fertilizers with slower release of nutrients can be divided into two classes:

1. Slow-Release Fertilizers (SRF)
2. Controlled (Regulated) Release Fertilizer (CRF).

CRF can comprise traditional soluble fertilizers, with quickly available nutrients, wherein following the process of granulation, prilling or crystallization, a protective coating with a layer for controlled release into soil influencing the solubility and release rate of nutrients is employed. A typical core component includes urea or N-P-K in various combinations, with or without addition of microelements.

Depending on type of the coating polymer and a method of preparation, there are three classes of fertilizers coated with polymer (Polymer Coated Fertilizer - PCF):
- a thermosetting copolymer is coated on the surface of the fertilizer;
- a thermoplastic polymer or copolymer is coated on the surface of the fertilizer;
two monomers are coated on the surface of the fertilizer, which polymerize together on this surface.

According to US 6,187,074 (2001), granules of the fertilizer can be coated with carboxyl-ethylene copolymer [75 to 95 % of ethylene and 10 % to 25 % of unsaturated carboxylic acids (acrylic, metacrylic, maleic, crotonic, fumaric)]. Tg value of the polymer ranges from -20 °C to +20 °C. Acrylamide, metacrylamide, N-metololacrylamide, N-butoxymetacrylamide, glycyl metacrylate and hydroxyethyl acrylate are also recommended as a comonomer to ethylene. The preferred melting point of the polymer is above 110 °C. The coating (layer) of the copolymer makes between 2 % and 10 % w/w of the granule. Lignin, starch or cellulose are added in order to control discharging of nutrients. Coating with copolymer occurs at the temperature between 30 °C and 70 °C. SiO2 or TiO2 is added after coating the layer of the polymer in order to prevent sticking the granules together.

A hygroscopic polymer (sodium polyacrylate, acrylic acid-vinylalcohol copolymer, polymers inaculated with starch, carboxymethylcellulose) can be coated on the fertilizer granules as a first step, and than polyurethane resin (US 6,358,295; 2002). Polyurethane resin will result from the reaction of isocyanate (e.g. toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate) and polyol (propylene glycol, trimethylolpropane, polytetramethylene ether glycol). The ratio of groups -NCO/-OH in the employed isocyanate and polyol is typically 0.9:1:2. NaOH, urea or triethylene diamine can be added to harden the polyurethane resin. The amount of hygroscopic polymer ranges between 1 and 20 WU (weight units) per 100 WU of urethane resin. The urea is heated to 70 °C, hygroscopic polymer is added, followed by dispersion and adding of isocyanate, polyol and hardener.

A polymer component of the coating can also comprise a polysaccharide dispersed in resin: cellulose, starch or sugars: glucose, fructose, xylose, arabinose (US 102,829; 1993). Oxidized starch, alkyl or hydroxyalkyl ether starch, starch modified by phosphoric acid, nitric acid, succinic acid, carboxymethylated starch, hydroxyalkylated starch, cationic starch and cellulose derivatives: carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, methylcellulose and carboxymethylcellulose are also applicable.
Carboxymethylcellulose is recommended. A vinylidene-chloride polymer, copolymer of vinylidene chlorid with ethylene, propylene, butene, ethylenevinyl ketone, vinylchloride or vinylideneacrylated copolymer can be used as a resin. Adding of powder polysaccharide or sugar makes 0,5 % to 20 % w/w of the resin. Water-unsoluble and sparingly soluble filler, e.g. talc, CaCO₃, S₁Ο₂, sulphur, zeolite, is added to the polymer mixture. Adding of the filler makes 20 % to 70 % w/w of the resin. The polymer component of the coating is dissolved on the organic solvent and sprayed at the granular fertilizer. After coating of the particles the solvent is evaporated due to hot air and the coating hardens. Duration of the controlled dissolving of the fertilizer is 26 to 315 days.

Slowly soluble nitrogen fertilizer can also be prepared by copolymerization of acrylic acid and maleic anhydride (dihydro-2,5-dioxofurane) using N,N-methylenebisacrylamide as a cross-linking agent in water environment in the presence of urea, ammonium peroxydisulphate and sodium sulfite as an initiator (Liu M., Liang R., Zhan F., Liu Z., Niu A., 2006: Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties, Research Article, Department of Chemistry, Lanzhou University, China). The product was cross-linked on its surface with trihydroxymethylpropane glycidol ether for improving the slow dissolution and an ability to retain water. The content of nitrogen in the synthetized fertilizer was 28.5 % and absorption of water cca 900 g/g in distilled water and 180 g/g in tap water. On the basis of the results of testing the rate of dissolution of nitrogen and absorption of water, it was found out that the surface cross-linked product provides not only for slow dissolution of nitrogen fertilizer, but also for a high capacity of retaining the soil humidity. The fertilizer could be utilized in dry regions.

The granules of fertilizer can first of all be coated with a layer of wax, than the material based on alkyd resin and a substance capable of swelling (JP 08151286; 1994). The urea (diameter 3.3 mm) is heated to 70 °C and the paraffin wax is sprayed at this temperature (60 °C). The wax layer makes 6.2 % w/w of the coated granule. Than the second layer, consisting of the mixture of alkyd resin on the basis of soya oil, tung oil and absorbing resin on the basis of sodium polyacrylate (Aqua Keep 10 SH) at the ratio of 95:5, is sprayed. This layer makes 8.1 % w/w of the coated granule. Such a surface-treated urea releases 8 % of
nitrogen after 30 days in water and 75 % after 120 days.

The fertilizer granules can also be coated with thermoplastic resin and than by a substance selected from the group comprising other thermoplastic resins, heat-hardening resins or inorganic substances (JP 0731 5975; 1994). Granules of urea having diameter of 3.3 mm were coated with wax and than by a mixture of alkyd resin, tung resin, pentaerythritol linolane and metallic soap.

The patent JP 07033575 (1993), presents granules coated with mixture based on oil modified resin (based on soya oil), unsaturated oil with conjugated double bonds (palm oil, tung oil, tall oil), pentaerythritols (anhydrid of maleic or phthahlic acid), metallic soap and amino resin (melamine resin, benzoguanamine resin, glycoluryl resin). No organic solvents were used in surface treating. The rate of releasing the nutrients from the coated granules was regulated by a type and amount of the employed amino resin. The amino resin was tested either as an upper layer of the coating in case of a two-layer coating, or in the mixture with alkyd resin in case of a one-layer coating.

In JP patent 06056567 (1992) the coating mixture contains an oil modified alkyd resin, unsaturated oil with conjugated double bonds and wax as the main component. The granules of urea having diameter of 3.3 mm were coated with mixture of soya oil modified alkyd resin (30 % w/w), tung oil (50 % w/w), pentaerythritol ester of linoleic acid (15 % w/w), metallic soap (3 % w/w) and conditioner (2 % w/w).

The fertilizer granules in EP 520456 B1 (1991) are also coated with mixture containing an oil modified alkyd resin and unsaturated oil with conjugated double bonds. The metallic soap can be present as well. The coating mixture contains soya oil based alkyd resin (30 % w/w), tung oil (49 % w/w), pentaerythritol ester of linoleic acid (15 % w/w), zirconium octylate (1.2 % w/w), cobaltous octylate (1.2 % w/w), manganous naphthenate (0.6 % w/w) and an anti-crusting agent (2 % w/w). After its heating the mixture was sprayed on the fluidized urea.

In JP patent 021 11686 (1988) the coating mixture contains the heat-hardening resin with terminal carboxyl group and a filler, e.g. talc. The concentration of filler in the mixture is between 5 and 25 % w/w. The fertilizer granules, comprising 20 % N and 10 % K₂O, were coated with mixture of alkyd
resin based on soya oil and talc (5.9 and 1.5 % w/w). Duration of releasing 80 % of the nutrients was 96 days.

The fertilizer with gradual release of nutrients was prepared by coating the fertilizer granules with mixture of resin based on oil modified phthalic acid and miscible oil resin (JP 630951 89; 1986). Resinoid varnish modified by soya oil based on phthalic acid (250 WU) was mixed with aromatic oil resin (25 WU) in order to obtain the coating mixture. The fertilizer granules (1 kg) containing N 18 % and K₂O 16 % were poured into the rotary drum and the coating mixture was sprayed on the granules through jets at the temperature of 60 to 100 °C. The percentage of the released ammonia nitrogen from the fertilizer in water on Day 10, 30, 50, 80 and 100 was 13 %, 34 %, 52 %, 71 % and 79 %. In case of fertilizer granules coated only with oil resin, 100 % N was released after 10 days.

The polymer for coating the surface of the fertilizer granules can also be obtained by reaction of polyisokyanate and alkyd resin modified by sorbitol fatty acid ester (JP 2008222536; 2007). The mixture of alkyd resin, containing 22 % of castor oil, 8 % of oleic acid, 16 % of adipic acid, 24 % of trimethylolpropane and 30 % of tristearate sorbitol, was blended with catalyst and heated. The urea granules (1 kg) in the centrifugal rotary granulating machine were heated to 70 °C, and the alkyd resin (4 g) and Sumidur 44V10 (2 g) as a polyisocyanate component were sprayed on them separately through two nozzles. When the resin hardened, the process of spraying the alkyd and polyisocyanate was repeated until the coating layer made 10 % w/w of the coated urea. The polymer coating showed biological degradability of 12.5 % and 88.3 % of nitrogen was released after 130 days. Similar granules coated with mixture based on alkyd resins without tristearate sorbitol showed biological degradability of only 2.5 % and 93.6 % of nitrogen was released after 40 days.

According to patent CN1 01289349 (2008) CRF consists of the core (fertilizer) and the coating containing sulphur on the surface of the granule, and on the surface of the sulphur there is a polymer film based on water-soluble alkyd resin. The amount of sulphur and polymer film is between 5 and 30 %, or between 0.5 and 10 % w/w of the coated fertilizer. The water-soluble alkyd resin contains an alkyd polymer having the acid value of 10 - 150 mg KOH/g of the resin. The alkyd pre-polymer is obtained by polycondensation of unsaturated conjugated
vegetable oil or fatty acid of vegetable origin with synthetic fatty acid or its
anhydride. The coating can also contain inorganic layer (montmorillonite, chalk,
kaoline, talc).

Controlling of releasing the nutrients also depends on the employed
coating. In case of alkyd resins the releasing is obtained by different composition
of the coating or its thickness. In case of polyurethane resins, but also many other
types of resins and thermoplastic polymers, the releasing is controlled mainly by
temperature, wherein the soil humidity, pH, weather or microbiological activity
have only a weak influence on releasing. In case of polyethylene coatings a part
of low permeable polyethylene is replaced by highly permeable polymer, e.g.
ethylene-vinylacetate.

The principal problem of using the alkyd resin for coating the granules
results from its low glass transition temperature (Tg) and thus a lower resistance
of the film against water. The low Tg also causes a strong stickiness of the resin
in its original state. Therefore, individual granules of the fertilizer get stuck
together during coating. When the resin hardens, it is possible to separate
individual granules, but the coating gets damaged. Due to this all, the nutrients are
not sufficiently utilized by plants and therefore the loss of nutrients is significant. In
order to avoid sticking the granules together during the coating process, it is
recommended to add a native vegetable oil (palm, rape, castor, linseed oil).

However, if the oil does not become a part of the polymer chain, it can be
degraded under certain conditions and thus the quality of the coating deteriorates.

These and other disadvantages of the above methods are removed by
application of the present invention.

Summary of the Invention

A significant part of the above deficiencies is removed by the granular
fertilizer with controlled release of nutrients according to the present invention,
which is based on the fact that it can be prepared by coating the fertilizer granules
with a mixture on base of alkyd resin containing cross-linkable functional groups
having a mean molecular weight between 500 and 2000. The alkylds are classified
as polyesters and are prepared from anhydrides of acids (anhydrid of phthalic
acid, maleic acid) and polyols (glycerol, pentaerythritol) in the presence of
unsaturated fatty acids (castor, soya, linseed oil), which contribute to drying of the
film on the air. With respect to the existence of double bonds in acids, the oils
react with oxygen in the air and individual components of the coating are mutually
cross-linked. In order to speed up drying of the coating, calcium salts, zirconium
salts or cobaltous salts of octyl acid or naphthenic acid, metallic soaps and etc.
can be added.

In order to increase the resistance of the alkyd resin film against water, it is
is possible to add amino resins (urea resin, melamine resin, benzoguanamine
resin) [JP 07033575 (1993)]. Amino resins have a significantly higher Tg value
than alkyd resin, and therefore they increase the hardness of the film after its
solidification. According to the said patent it is preferred to use the alkyd resin
either as an inner coating of the granule, on which amino resin film is then coated,
or to use the amino resin for coating the granules in the mixture with alkyd resin.
However, in both the above cases the amino resin does not react directly with
alkyd resin based on tung oil, but it is self-condensated. As no mutual cross-
linking between alkyd resin and amino resin occurs, the quality of the coating can
deteriorate during longer storage of the coated granules.

It is possible to avoid the problems with quality of the fertilizer coating
based on alkyd resin by creating conditions, which would enable cross-linking of
alkyd resin and amino resin during coating of the granules. This process not only
considerably reduces the time of drying the mixture on the surface of granules
(from 60 minutes to 10 minutes), but also significantly reduces the necessary
proportion of the coating in the weight of the coated granules (see examples).

In order to reach the cross-linking, it is necessary that the alkyd resin
contained functional groups able of cross-linking (hydroxy, amino, epoxy groups).
As the esterification process during production of the standard alkyd resin is
brought to a high degree of conversion, there is only a minimal amount of free
hydroxy groups in the structure of the resin molecule.

A functional group can be incorporated in the structure of the alkyd resin for
example by its grafting with functional monomer (2-hydroxyethylmethacrylate, N-
methylolacrylamide, ethyleneglycoldimethacrylate, etc.). This variant of treating
the alkyd resin is enabled by oil present in the resin, which oil contains acids (e.g.
oleic acid, linoleic acid) having one or two double bonds, and these bonds are able of polymerisation. Organic peroxide (tert-butylhydroperoxide, tert-butylperbenzoate) can be used as an initiator. Grafting is performed at the temperature of 120 to 180 °C.

As a second variant, alkyd resin based on castor oil can be used. Castor oil consists predominantly of triglycerides of ricinoleic acid. This acid contains in its molecule a reactive -OH group, suitable for cross-linking with methylol groups of amino resin.

As the grafting process requires an additional technological step, it seems to be economically more favourable that in the coating there is applied an alkyd resin preferably of pentaerythrite polyester of orthophthalate type, modified by fatty acids of castor oil, available on the market without any further treatment. The amount of alkyd resin in the mixture for coating was in the range between 30 and 80 % w/w.

An amino resin containing reactive methylol groups (-CH₂-OH) was used as a suitable hardener of the alkyd resin based on castor oil. Concentration of amino resin in the mixture with alkyd resin was in the range between 1 and 30 % w/w. From among amino resins, urea-formaldehyde or melamine-formaldehyde resin, preferably methylolated, i.e. with higher reactivity, can be used as a hardener. It was found out that in order to prolong the period of processability of the mixture of alkyd and amino resin, the amino resin can be dissolved in butylalcohol, preferably butylacetate, before it is added to the alkyd resin.

It was found out that in order to avoid sticking the granules together during the coating, it is suitable to add vegetable oil (palm, rape, castor, linseed oil). An additional adding of vegetable oil in the mixture of alkyd resin and amino resin is in the range between 1 and 40 % w/w. It was found out that castor oil can preferably be used in the presence of amino resin in order to avoid sticking. This oil will react with amino resin and thus prevent degradation of the oil during storage of the coated fertilizer.

The coating mixture can be prepared in the container with mixer at the room temperature. After weighing the alkyd resin, the amino resin dissolved in butylalcohol is added gradually. The mixture is thoroughly stirred and then vegetable oil is added. After homogenization the coating mixture is prepared for
coating, which is performed by spraying 3 to 20 doses of the coating mixture in the rotary cylindrical container or fluid apparatus at the temperature between 60 and 120 °C, preferably between 80 and 100 °C. It is desirable that the resulting granule contained the layer based on the coating mixture in the amount of 6 to 25 % w/w of the total weight of the coated granule, preferably 9 to 15 % w/w.

Coating under laboratory conditions was performed in Aeromatic AG jet drier and the coating mixture was applied by means pressured air. The granules were carried away and dried by the flow of warm air from the lower, narrower part of the column. Dosing of the coating mixture into the air flow was provided by syringe. The coating mixture was sprayed in 4 to 10 even doses. Drying was carried out at the temperature of 70 to 120 °C. Each following dose of the mixture was sprayed after complete hardening of the previous dose on the surface of granules, namely at the intervals of 5 to 15 minutes. The resulting film has a character of cross-linked polymer, like in case of thermosets, which reduces the thermal sensitivity of penetrability of water through the film.

**Examples**

The rate of releasing the nutrients from the coated fertilizer was tested in duplicator container with fertilizer granules integrated in the layer of sand. After closing the container the duplicator was poured with distilled water, which was flowing through the sand layer with granules and was soaking it. Water for analysing the concentration of released nutrients was retained in glass flask after flowing through the sand layer with samples of granular fertilizer. The water soaking cycle was repeated in relevant time intervals.

Granules produced by Agrofert Duslo a.s. Šal'a, namely Duslofert Extra NPK 14-1 0-20 (+7S), and granulate of ammonium nitrate with finely milled dolomite (ammonium nitrate, 27 % N) were used for coating. The diameter of granules was between 2 and 5 mm. The granules were coated with mixtures based on alkyd resin according to Examples 1 to 6.

**Methods of Evaluating the Fertilizers with Controlled Releasing of Nutrients by Water Testing**
Prepared samples of granular fertilizer with controlled releasing of nutrients (40 g) were tested in duplicator container, incorporated in the layer of sand. A fine, washed and dried sand was used, i.e. inert material without any organic substances. The container was closed, water pump of thermostat for circulation circuit of warming the jacket was switched on. Temperature of circulation water was set on a constant value of 23 °C. The same was done for the temperature of water in thermostat and of distilled water for extraction of nutrients from the coated samples.

The period of dosing the water (500 ml) through the filling with a sample of fertilizer was optimalized to cca 120 minutes. The rate of dosing the water during the first approximately 5 minutes was set to max. 14 ml/min. After creating the surface on the sand in the container, this surface was maintained at the dosing rate range of 3.5-4 ml/min.

Water intended for analysing the concentration of releasing the nutrients was retained in glass flask after having gone through the sand layer with a sample of fertilizer.

**Examples 1 - 5**

The granules of nitrogen fertilizer (ammonium nitrate with finely milled dolomite) were used for preparing the coated fertilizer according to the present invention. The coating mixtures of the following compositions were prepared for coating 1 kg of granules:

1. 63.6 % alkyd resin (R 45/65 BC), 18.2 % amino resin (Luwipal), 9.1 % castor oil and 9.1 % butylalcohol
2. 69.2 % alkyd resin (R 45/65 BC), 15.4 % amino resin (Luwipal), 7.7 % castor oil and 7.7 % butylalcohol
3. 73.3 % alkyd resin (R 45/65 BC), 13.3 % amino resin (Luwipal), 6.7 % castor oil and 6.7 % butylalcohol
4. 76.5 % alkyd resin (R 45/65 BC), 11.7 % amino resin (Luwipal), 5.9 % castor oil and 5.9 % butylalcohol
5. 78.9 % alkyd resin (R 45/65 BC), 10.5 % amino resin (Luwipal), 5.3 % castor oil and 5.3 % butylalcohol.
Granules of ammonium nitrate were heated to 100 °C by the flow of hot air. The coating mixture was sprayed gradually. After coating the fertilizer granules the samples underwent water testing. The course of releasing the nitrogen from individual samples of granular fertilizer is shown in Table 1.

Table 1: Water testing of samples of granular fertilizer (GF) prepared according to Examples 1 - 5

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Day</th>
<th>Concentration of released N [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GF with mixture No. 1</td>
</tr>
<tr>
<td>1</td>
<td>1.</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>2.</td>
<td>4.8</td>
</tr>
<tr>
<td>3</td>
<td>4.</td>
<td>6.7</td>
</tr>
<tr>
<td>4</td>
<td>7.</td>
<td>8.2</td>
</tr>
<tr>
<td>5</td>
<td>17.</td>
<td>48.1</td>
</tr>
<tr>
<td>6</td>
<td>28.</td>
<td>95.3</td>
</tr>
<tr>
<td>7</td>
<td>56.</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>84.</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>112.</td>
<td>-</td>
</tr>
<tr>
<td>% w/w of the coating</td>
<td>7.2</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**Example 6**

Granules of the combination fertilizer Duslofert Extra NPK 14-1 0-20 (+7S) were used for coating according to the present invention. A coating mixture containing 66.6 % of alkyd resin (R 45/65 BC), 16.8 % of amino resin (Luwipal), 8.3 % of castor oil and 8.3 % of butylalcohol was prepared. The dry basis was 67 %. The following doses of mixture were tested for coating the granules:

1. 150 g/1 kg of granules
2. 140 g/1 kg of granules
3. 130 g/1 kg of granules
Granules were heated to 100 °C by a flow of hot air. The coating mixture was sprayed gradually. After coating the fertilizer granules the samples underwent water testing. The measured values of the released nitrogen depending on time are shown in Table 2.

Table 2: Water testing of samples of granular fertilizer (GF) prepared according to Example 6

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Day</th>
<th>Concentration of released N [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GF with mixture No. 1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>17</td>
<td>17.5</td>
</tr>
<tr>
<td>6</td>
<td>28</td>
<td>56.1</td>
</tr>
<tr>
<td>7</td>
<td>56</td>
<td>75.6</td>
</tr>
<tr>
<td>8</td>
<td>84</td>
<td>89.1</td>
</tr>
<tr>
<td>9</td>
<td>112</td>
<td>94.2</td>
</tr>
<tr>
<td>% w/w of the coating</td>
<td></td>
<td>8.5</td>
</tr>
</tbody>
</table>

Tables 1 and 2 show the results of water testing of the coated granules of nitrogen and combination fertilizer with a mixture of alkyd resin based on conjugated esters of orthophthalate acid and pentaerythritol, containing castor oil and melamine formaldehyde resin. Tables 1 and 2 demonstrate that by cross-linking of alkyd resin with amino resin unlike physical drying alkyd resins on the surface of granules (see Examples 7 to 11), it is possible to achieve gradual releasing of nutrients from the fertilizer at a lower ratio of the coating on the weight of the coated granules (8 to 12 % w/w).
Example 7

Granules of the combination fertilizer Duslofert Extra NPK 14-1 0-20 (+7S) were used for coating according to the present invention. A coating mixture containing 69.4 % of alkyd resin (CHS Alkyd 870), 19.8 % of amino resin (Cymel 303), 10.3 % of metylester of rape oil, 0.3 % of p-toluenesulphone acid and 0.2 % of cobaltous octylate was prepared. The dry basis was 97 %. The following doses of mixture were tested for coating the granules:

1. 180 g/1 kg of granules
2. 150 g/1 kg of granules
3. 100 g/1 kg of granules

Granules were heated to 100 °C by the flow of hot air. The coating mixture was sprayed gradually. After coating the fertilizer granules the samples underwent water testing. The measured values of the released nitrogen depending on time are shown in Table 3.

Table 3: Water testing of samples of granular fertilizer (GF) prepared according to Example 7

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Day</th>
<th>Concentration of released N [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GF with dose No. 1</td>
</tr>
<tr>
<td>1</td>
<td>1.</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>2.</td>
<td>3.7</td>
</tr>
<tr>
<td>3</td>
<td>4.</td>
<td>8.1</td>
</tr>
<tr>
<td>4</td>
<td>7.</td>
<td>16.8</td>
</tr>
<tr>
<td>5</td>
<td>17.</td>
<td>37.1</td>
</tr>
<tr>
<td>6</td>
<td>28.</td>
<td>66.8</td>
</tr>
<tr>
<td>7</td>
<td>56.</td>
<td>85.4</td>
</tr>
<tr>
<td>8</td>
<td>84.</td>
<td>99.1</td>
</tr>
<tr>
<td>% w/w of the coating</td>
<td>17.1</td>
<td>14.5</td>
</tr>
</tbody>
</table>
Table 3 shows the results of water testing of the coated granules of the combination fertilizer (Duslofert Extra NPK 14-1 0-20 (+7S)) with a mixture of alkyd resin based on conjugated esters of isophthalate acid and pentaerythritol, containing tall oil and melamine formaldehyde resin with high degree of alkylation. No cross-linking occurs in the process of coating the granules, because the employed alkyd resin does not contain cross-linkable functional groups. Instead, the alkyd resin undergoes the physical process of drying out catalyzed by metallic soap, and the melamine resin is self-condensated due to acidic catalyst.

**Example 8**

Table 4: Water testing of samples of granular fertilizer with a mixture of alkyd resin based on tung oil and cobaltous octylate [US 531 0785 (1994)]

<table>
<thead>
<tr>
<th>Measurement</th>
<th>% w/w of the coating</th>
<th>Concentration of released N (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Day 3</td>
</tr>
<tr>
<td>1</td>
<td>17.6</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>18.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 4 shows the water testing results for coated granules of nitrogen fertilizer (urea) with mixture of alkyd resin based on conjugated esters of linoleic acid and pentaerythritol, containing tung oil and cobaltous octylate according to US 5,310,785 (1994). No cross-linking occurs in the process of coating the granules. Instead, the alkyd resin undergoes the physical process of drying out catalyzed by metallic soap.

**Example 9**

Table 5: Water testing of samples of granular fertilizer with mixture of alkyd resin based on soya and tung oil and metallic soap [JP 6056567A (1994)]
Table 5 shows the water testing results for coated granules of nitrogen fertilizer (urea) with mixture of alkyd resin based on conjugated esters of linoleic acid and pentaerythritol, containing soya and tung oil and metallic soap according to JP 6056567A (1994). No cross-linking occurs in the process of coating the granules. Instead, the alkyd resin undergoes the physical process of drying out catalyzed by metallic soap.

Example 10

Table 6: Water testing of samples of granular fertilizer with mixture of alkyd resin based on soya and tung oil, metallic soap and wax [JP 8151286A (1996)]

<table>
<thead>
<tr>
<th>Measurement</th>
<th>% w/w of the coating</th>
<th>Concentration of released N (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Day 30</td>
</tr>
<tr>
<td>1</td>
<td>13.6</td>
<td>33.0</td>
</tr>
<tr>
<td>2</td>
<td>14.1</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Table 6 shows the water testing results for coated granules of nitrogen fertilizer (urea) with mixture of alkyd resin based on conjugated esters of maleine acid and pentaerythritol, containing soya and tung oil, metallic soap and wax according to JP 8151286A (1996). No cross-linking occurs in the process of coating the granules. Instead, the alkyd resin undergoes the physical process of drying out catalyzed by metallic soap.
Example 11

Table 7: Water testing of samples of granular fertilizer with mixture of alkyd resin based on soya and tung oil and metallic soap [JP 731 5975A(1995)]

<table>
<thead>
<tr>
<th>Measurement</th>
<th>% w/w of the coating</th>
<th>Concentration of released N (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Day 10</td>
</tr>
<tr>
<td>1</td>
<td>17.3</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>17.0</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>12.0</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 7 shows the water testing results for coated granules of nitrogen fertilizer (urea) with mixture of alkyd resin based on conjugated esters of linoleic acid and pentaerythritol, containing soya and tung oil and metallic soap according to JP 731 5975A (1995). No cross-linking occurs in the process of coating the granules. Instead, the alkyd resin undergoes the physical process of drying out catalyzed by metallic soap.

The process of physical drying out of the alkyd resin is time-consuming. However, due to cross-linking, a lower % of the coating (8 % - 12 %) is sufficient for reaching the required rate of releasing nitrogen, whereby the coating process becomes more economical.

Industrial applicability

The present invention can be used in production of granular fertilizers with controlled releasing of nutrients (PCF).
CLAIMS

1. Granular fertilizer with controlled releasing of nutrients, which fertilizer can be prepared by coating it with a mixture consisting of the alkyd resin containing cross-linkable functional groups with mean molecular weight between 500 and 2000 in the amount 30 to 80 % w/w, amino resin in the amount of 1 to 30 % and vegetable oil in the amount of 1 to 30 % w/w.

2. Granular fertilizer according to claim 1, characterized in that the amino resin is dissolved in butylalcohol, preferably in butylacetate.

3. Granular fertilizer according to any of claims 1 to 2, characterized in that the amino resin is the metyloled melamine formaldehyde resin.

4. Granular fertilizer according to any of claims 1 to 3, characterized in that the vegetable oil is the castor oil.

5. Granular fertilizer according to any of claims 1 to 4, characterized in that the coating mixture contains 66.6 % w/w of alkyd resin, 16.8 % w/w of amino resin, 8.3 % w/w of castor oil and 8.3 % w/w of butylalcohol.

6. Granular fertilizer according to any of claims 1 to 5, characterized in that the fertilizer is coated by gradual spraying of 3 to 20 doses of coating mixture, wherein the coating is performed in rotary cylindrical container or fluid apparatus at the temperature of 60 to 120 °C, preferably 80 to 100 °C.

7. Granular fertilizer according to claim 6, characterized in that the layer of the coating mixture makes 6 to 25 % w/w of the overall weight of the coated granule, preferably 9 to 15 % w/w.