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## PROSPECTS OF USING PET WASTE FOR ENVIRONMENTALLY FRIENDLY MINERAL FERTILIZERS

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**Abstract.** The article presents the technological possibility of using PET wastes for encapsulation of granulated mineral fertilizers. The schematic flowsheet is proposed to obtain film-forming composition. An encapsulated ammonium nitrate with predictable kinetics of fertilizer components release was obtained.

**Key words:** polyethylene terephthalate, wastes, encapsulated fertilizers.

### 1. Introduction

Polyethylene terephthalate (PET) is a strong, firm and light weight material of new generation. PET physical properties make it an ideal one to be used in different fields: production of packaging (bottles, aprons, etc.), films, fibers, structural elements. The used bottles are the main kind of PET waste. Currently, more than 10,000 tones of PET chips per month are imported in Ukraine. The bulk of material in the form of bottles is directed to the markets, so it eventually becomes waste. Only 1,000 tones of PET waste per month are recycled, the rest is stored at landfills and garbage dumps or piled up along roadsides [1, 2]. It is reasonable to study the use of PET waste for encapsulation of granular fertilizers. Encapsulated fertilizers are characterized by a high rate of mineral nutrients assimilation by plants. Hence, the required dose and multiplicity of applied fertilizers, as well as environment pollution by residual agrochemicals are reduced. Despite the advantages of encapsulated fertilizers in comparison with traditional ones, mainly nitrogen fertilizers are produced. The world production of encapsulated fertilizers is only 0.4 ÷ 0.5 % [3] in spite of a significant number of developed film-forming materials [4, 5]. The reason is a high cost compared to

usual granular fertilizers. Thus, the investigation of waste use for fertilizers encapsulation is an urgent problem, because the cost of fertilizers production will be reduced and economic attractiveness for agriculture will increase.

### 2. Investigation Materials

For the investigation we used PET package waste in the form of flakes and granular mineral fertilizer – ammonium nitrate. Polyethylene terephthalate is a polyester obtained via terephthalic acid polycondensation (Fig. 1).

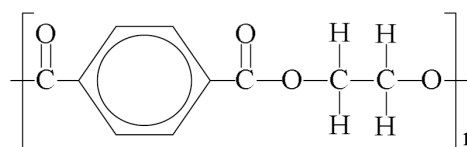


Fig. 1. Schematic drawing of PET molecule fragment

### 3. Results and Discussion

At the production of encapsulated mineral fertilizers the polymers are used as a basis of film-forming composition. Polymeric materials allow to obtain long-acting fertilizers with predicted properties and minimal thickness of the covering. The use of waste for encapsulated fertilizers production may be represented in the following way:

- collection of used PET products;
- primary processing of waste;
- obtaining of film-forming composition;
- encapsulation of granular fertilizers.

*Collection of used PET products.* PET waste is already formed during products manufacturing as technological residues or spoilages. This is industrial waste, its processing requires minimal costs, and as a rule, it is usually re-used at the enterprises as a feedstock. The main part of PET waste is formed after use of packaging. The sources of such waste formation cover a wide area. In this case, it is necessary to collect and deliver waste to the plant, where its primary processing takes place. In the city of Lviv separated collection of household waste is provided by means of waste sorting in different containers. The main bulk of material is obtained while collecting used bottles. Identification of the bottles is usually not difficult. All bottles for beverages are made of PET and bottles for other liquids have a special marking – a recycling symbol with “1”.

*Primary processing of waste.* The company “Halpet” is the main enterprise in the West region which collects and preprocesses PET waste. The primary processing includes the following. Originally pressed bales are broken into separate bottles and external heavy impurities are removed. Next, the bottles are sorted, crushed, they undergo air separation, after this they are washed in special bath using alkaline solutions and new detergents, floated, etc. Then the material is ground to obtain the commodity fraction, it undergoes secondary air separation and packed. Pure flakes are granulated, i.e. a high quality secondary crystal granule is obtained via complete melting of raw material, its filtration and granulation [1].

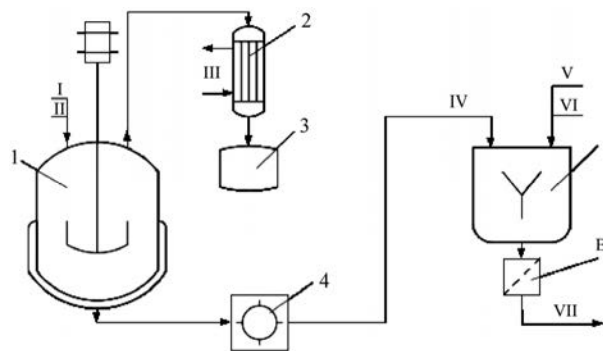
*Obtaining of film-forming composition.* The shell of encapsulated fertilizer granule contains various functional additives apart from polymer. The shell components mixing, as well as its applying over granule surface should be done in liquid state. This task may be solved in two ways:

- 1) by dissolving of desired components using solvents;
- 2) by components mixing in PET melt.

The use of melts as the film-forming shell requires corresponding equipment, where necessary temperature is provided. Since PET melting point is 280 °C, the use of melt leads to additional heat consumption. At the same time, it is not recommended to heat the nitrogen granulated fertilizers above 70 °C, due to their thermal decomposition [6]. The method using aqueous solutions has not mentioned shortcomings, though the expenditures for materials, evaporation and purification of air from solvent vapors increase. From the standpoint of ecology and material costs the application of aqueous solutions would be more preferable. However, PET is insoluble in water and many organic solvents. Within the temperature range of 40–150 °C it is dissolved in phenols and their alkyl- and chlorine-substituted compounds, aniline, benzyl alcohol, chloroform, pyridine, di-chloroacetic and chlorosulfonic acid, cyclohexanone, etc. To determine the molecular weight by viscosimetry

PET solutions with cresols, o-chlorophenols, phenol-tetrachloromethane are used [7]. To our mind, it is inexpediently to use acids or aromatic solvents to dissolve PET because they are aggressive and high toxic substances. This will lead to excessive material and energy costs while obtaining capsulated fertilizers and consequently reduce their availability for mass agricultural production.

To increase the PET waste solubility, its chemical modification by diethyleneglycol has been developed [8]. The essence of the process is alcoholysis of ground PET-packing at 493 K and vacuum distillation of ethylene glycol under the residual pressure of 20 kPa. The modification time is 3.5 hours. The obtained product is soluble in ethylacetate, carbon tetrachloride, etc. at the room temperature. This simplifies the obtaining of film-forming compositions and its cost as a result. We propose the principal flowsheet to prepare film-forming composition for encapsulation of granulated mineral fertilizers (Fig. 2).



**Fig. 2.** Principal flowsheet for preparation of film-forming composition:

- 1 – reactor; 2 – ethylene glycol condenser;  
 3 – ethylene glycol collector; 4 – chipper; 5 – mixer;  
 6 – screen filter; I – PET; II – diethylene glycol;  
 III – refrigerant; IV – modified PET; V – solvent;  
 VI – composite additives; VII – film-forming composition

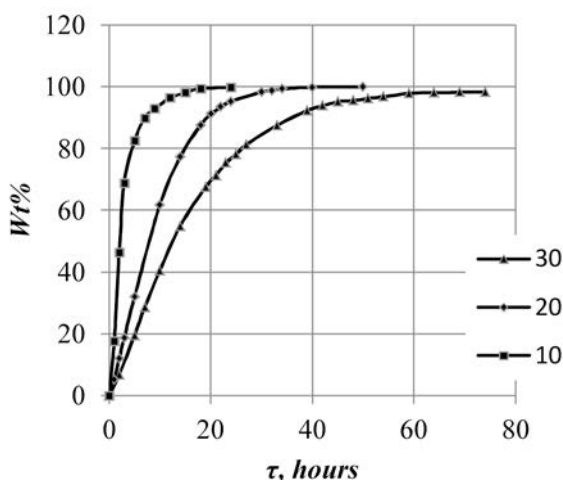
PET waste in the form of flakes and diethylene glycol is loaded into a reactor 1, where alcoholysis is carried out. Ethylene glycol formed during the reaction is taken off the reactor, condensed in the condenser 2 and directed to the collector 3. After the reaction end the product is reloaded into the chipper 4, where it is ground to the size of < 0.5 mm. The ground modified PET, solvent and composite additives are directed to the mixer 5. In our case we added hydrolytic lignin which provides the biological decomposition of the shell. Hydrolytic lignin is an artificial substance, waste of wood-pulp industry, residue of wood hydrolysis. Carbon tetrachloride was used as the solvent, because ethyl acetate decomposes while heated and forms ethyl alcohol and acetic acid. The solvent is fire-safe, inflammable and low-toxic one. The solution of film-forming composition obtained according to the mentioned scheme was used for encapsulation of granulated ammonium nitrate.

#### Encapsulation of granulated mineral fertilizers.

Granulated fertilizers should be encapsulated via shell sputtering over surface of particles being in fluidized state. This method is realized in the fluidized-bed apparatus. Such equipment is characterized by high intensity of heat-and-mass transfer during encapsulation and provides high quality of covering. The encapsulation of ammonium nitrate is carried out in the cylindrical fluidized-bed batch reactor under following conditions [9]:

- Air rate – 6.10 m/s;
- Flow rate of film-forming composition – 0.032 kg/s;
- Encapsulation time for 1 wt % of covering per fertilizer weight – 75 s;
- Temperature of fluidizing air at the reactor inlet – 70 °C.

The important quality coefficient of applied covering is uniformity of shell thickness. It allows to predict the intensity of components release into the soil and produce encapsulated fertilizers with necessary term of action. According to above-mentioned conditions, we encapsulated ammonium nitrate by modified PET: lignin mixture (ratio 8:2). The covering value was 10, 20 and 30 wt% relative to the fertilize weight. The encapsulation quality was controlled by the nature of release curve [10]. The kinetics of components release from the encapsulated particles was studied by conductimetric method. The experimental results are represented in Fig. 3.



**Fig. 3.** Kinetics of ammonium nitrate release from the encapsulated particles with different covering values, wt %

One can see from Fig.3 that the kinetic curves of the release process are smooth. It is the proof of uniform high-quality covering which allows to produce fertilizers of prolonged action with controlled time of release.

## 4. Conclusions

The technological possibility of using PET wastes for the encapsulation of granulated mineral fertilizers is examined on the basis of theoretical and experimental investigations. The modified PET/hydrolytic lignin film-forming composition has been obtained. The granulated ammonium nitrate has been encapsulated in the fluidized-bed reactor. The covering uniformity has been confirmed by the experiments which allows to produce encapsulated fertilizers with preset properties.

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