Journal of Agricultural Science and Technology A 9 (2019) 338-343

doi: 10.17265/2161-6256/2019.06.002



# Complex Preparations for the Protection Potato on the Basis of Tebuconazole

Khalikov Salavat Samadovich<sup>1</sup>, Malyuga Anna Anatolievna<sup>2</sup> and Chulikova Natalia Sergeevna<sup>2</sup>

- 1. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Science (RAS), 28, Vavilova str., Moscow 119991, Russia
- 2. Siberian Research Institute of Agriculture and Agricultural Chemicalization of the Siberian Federal Scientific Center for Agrobiotechnology of RAS, Krasnoobsk, Novosibirsk District 630501, Russia

**Abstract:** Among the various methods to protect potatoes from common diseases, the most economical and environmentally friendly is tuber dressing. Based on the tebuconazole, thiram and benzimidazole fungicides, protectants (in the form of solid dispersions and suspensions) have been developed for use on potatoes against various diseases. The solid-phase mechanochemical modification of selected fungicides with the help of water-soluble polymers made it possible to obtain supramolecular complexes that possessed high biological activity with a reduced dosage of active substances 10 and more times due to their influence on the properties of cell membranes. An alternative approach—the development of stable suspension forms for these fungicides without the use of traditional formative substances (stabilizers, emulsifiers, film formers, etc.)—allowed for the practical use of innovative products in the form of suspension concentrates. The analysis of the quality indicators of the obtained multicomponent environmentally friendly protectants made it possible to select the most promising of them, the biological tests of which indicated a decrease in the number of tubers of patients with dry rot 1.6-2.0 times in comparison with the control variant, and they were also more effective than the standard preparation (Colfugo Super, SC 60) 1.2-1.3 times. The proposed preparations significantly reduced the development of rhizoctoniosis in the period of sprouting 5.8-7.3 times or the plants were completely healthy, and in the budding-flowering stage 2.7-5.5 times. The preparations provided a reliable yield increase, and also reduced the weight percentage of unsuitable tubers and significantly increased the yield of healthy tubers.

Key words: Fungicides, solid dispersions, suspensions, potatoes, biological efficacy.

## **Abbreviations**

Tebuconazole TBC **TMTD** Thiram RMCCarbendazim Naphthalic anhydride NA SD Solid dispersions LE-101 Impact-type mill SC Suspension concentrate AG Arabinogalactan HES Hydroxyethyl starch pVpPolyvinylpyrrolidone

Active substance

# 1. Introduction

Reducing the incidence of disease of plants can be achieved with the help of various chemicals that

**Corresponding author:** Khalikov Salavat Samadovich, Ph.D., research fields: technology of biological active substances; formulations of pesticides and anthelmintics.

penetrate into plants, assimilate them, bring influence to bear on the metabolism, thereby increasing resistance to pathogens. Fungicides, growth regulating agents, antibiotics, macro- and micro-elements can cause chemical immunization [1].

Fungicides of the complex-immunizing effect or the products of their decomposition change the plant's metabolism toward increasing resistance to diseases not only in the year of processing, but also in subsequent generations, which give reason to attribute this phenomenon to the type of artificial immunity.

The annual high infection of seed tubers make necessary preplant treatment of tubers [2]. This technique provides the maximum effect with minimal negative impact on the components of agrocenosis. For direct depression and destruction of pathogens, contact and systemic chemicals are mainly used,

which reduce viability or cause death of the pathogen, interrupting its infectious cycle. This is achieved by the destruction of infection in tubers and their protection pathogens of soil-tuberous against infections, both during storage and during germination. This technique to some extent also prevents the new crop tuber infection.

Potatoes are diseased by a wide range of fungal, viral, bacterial and non-infectious diseases, due to the characteristics of the culture (carbohydrate-rich tubers and tops; defeat of pathogens before germination, during the growing season and during storage; vegetative reproduction), changes in the biological attributes of pathogens (increasing their plasticity, adaptability pathogenicity). Among the many diseases of potato, dry rot during storage (annual losses of 15%-25%), and black scaf (annual losses of 45%-50%) occupy one of the first places in terms of distribution and harm caused by them [3]. One of the most effective methods in the fight against potato diseases is a chemical. However, it must be borne in mind that the disinfectants used must comply with sanitary and hygienic and environmental safety requirements, namely, the high efficacy of the preparations must be combined with a low hazard to warm-blooded animals and the environment [1].

The aim of the work was to develop methods for producing multicomponent protectants based on TBC and other fungicides, studying their biological efficacy against pathogens of dry rots during storage and black scab of potatoes during the growing season, as well as their impact on crop yields.

## 2. Materials and Methods

As fungicidal components of the study were selected:

- TBC, a.s. of which (RS)-1-p-chlorophenyl-4,4 -dimethyl-3-(1H-1,2,4-triazol-1-yl-methyl)pentan-3-yl. Colorless crystals, well soluble in organic solvents, poorly in water (1 mg/L) [4].
  - TMTD, a.s. of which bis (dimethylthiocarbamyl)

disulfide. White or light gray powder. Well soluble in most organic solvents, poorly in water (16 mg/L) [4].

- BMC, a.s. of which N-(benzimidazolyl-2)-O-methylcarbamate. Grayish powder, poorly soluble in water (8 mg/L) and many organic solvents [4].
- Benomil, a.s. which N-[1-(butylcarbamoyl) -benzoimidazolyl-2]-0-methylcarbomate. White crystalline substance with a faint irritating odor. Practically insoluble in water (< 2 mg/L) and most organic solvents [4].

The fungicides were chosen for the study, like the majority of biologically a.s. used in practice, belong to the class of poorly or insoluble in water and physiologically active media [5], which implies the use of excessive dosages of a.s. and thus increases the price of the drug and increases its toxicity for the environment. To increase the solubility of poorly soluble drug substances, various methods are known, including physical, physicochemical, etc. [6]. An innovative method of mechanochemical modification of poorly soluble medicinal substances by the joint mechanical treatment of their substances with water-soluble polymers has been proposed [7]. Obtained, in the described conditions of the mechanochemical of **TBC** modification with water-soluble polysaccharides, SD had increased solubility in water and high fungicidal activity compared to the original TBC while reducing the recommended dosage by 5-10 times, which was explained by the formation of supramolecular complexes [8]. This method was used to create protectants for processing potatoes based on selected fungicides. Thus, polymers (AG, HES, PVP) were used to increase the solubility of BMC, and the process of SD obtaining was carried out with the combined treatment of BMC with these polymers in impact-type mill LE-101. The resulting SD was investigated for water solubility, dispersion, as well as by infrared (IR) spectroscopy and thermal analysis to confirm the formation of intermolecular guest-host complexes [9]. The analysis of the solubility of BMC and its SD showed that they all have increased to 20 or more times the solubility in water compared with the original substance of BMC, which implies a corresponding increase in biological activity.

# 3. Results and Discussion

Biological studies of protectants based on BMC showed that they all had higher efficacy against pathogens of dry rot during storage (biological efficacy of 92%-93%) than the standard fungicide protectant—Colfugo Super, SC 60 (biological efficiency of 67%). The weight percentage of diseased tubers affected by dry rot storage in the variants with experimental preparations based on BMC was lower by 12.5-14.5 times in comparison with the control variant, and 4.1-4.8 times compared with the standard. Studies have also shown that the preparations were effective against the black scab pathogen of potatoes, but this figure varied depending on the date of their use. All the studied preparations applied to the tubers, both in autumn and spring, to the full germination phase compared with the control significantly reduced the development of rhizoctoniosis by 1.5-8.0 times and 2.3-8.0 times, respectively. For Colfugo Super, SC 60 this indicator in the first case was 1.8 times, in the second—2.6 times. In addition, the protectants based on the BMC had an impact on the biometric indicators of the culture (length of plants, their mass, etc.). So they increased the length of plants—by 3.0-4.2 cm/plant in comparison with the control. Autumn treatment of tubers with protectants significantly increased this indicator by 0.8-1.5 cm, in comparison with spring treatment. Under the influence of experimental compounds, the mass of plants increased by 13-47 g while Colfago Super, SC 60 increased this indicator by 23-24 g/plant. In general, the complex effect of protectants based on BMC on the development of the disease, development and growth of potato plants led to an increase in crop yield by 1.52-4.75 t/ha [10]. The same results were showed for anthelmintic drugs by creating water-soluble compositions of lipophilic drug compounds [11]. It was demonstrated an increase in the solubility and penetration ability of TBC into plant objects [12].

Taking into account the prospects of SC of fungicidal preparations [13], suspension forms of the fungicides studied have been obtained in an environment of a 2% aqueous polymer solution without adding traditional formative components during mechanical treatment for 1-5 h. To obtain protectants with a complex action, multicomponent fungicidal suspensions of TBC and its combinations with BMC and TMTD were prepared under conditions.

The resulting SC was studied on:

- The prevalence of dry rot in the winter, when treating tubers with protectants before putting it in storage;
- The peculiarity of the formation of the phytosanitary situation in the planting of potatoes in relation to black scab in the treatment of tubers with protectants before planting the crop;
- The productivity of culture under the action of developed protectants.

The objects of research were selected potatoes (Solanum tuberosum L.), black scab of potato (Rhizcontia solani Küch.), dry rot during storage (Fusarium spp. and Phoma exiqua sp.).

Studying the effect of suggested protectants on the disease excitant of fusarium and fomoz showed that the developed preparations—SC-210 (composition: 10 g/L TBC; 160 g/L TMTD), SC-211 (composition: 7.2 g/L TBC; 121 g/L TMTD; 21.1 g/L BMC) and SC-213 (composition: 14 g/L TBC; 233 g/L TMTD; 58 g/L NA) had a rather high efficiency during storage, when the weight percentage of tubers with dry rot was correspondingly lower in 1.6, 2.0 and 1.9 times in comparison with the control variant, and they were more effective than the standard Colfugo Super, SC 60 1.3-1.4 times [14].

The study of the action of preparations against black scab of potato showed that protectants SC-210 and SC-213 influenced the development of the

disease, but their effectiveness varied depending on the date of their use. So, they significantly reduced the development of the disease in the period of sprouting 5.8-7.3 times or the plants were completely healthy, and in the budding-flowering phase 2.7-5.5 times. The efficacy of the standard protectant was lower by 2.6 times and 2.3 times, respectively. In general, the effectiveness of disinfectants was higher during spring treatment of planting material, in which the development of black scab on plants in the phase of full sprouting was significantly lower by 2.1 times, and during budding-flowering—1.3 times when using disinfectants before planting.

The positive effect of the protectants on the development of the disease, the development and growth of potato plants was established, which led to an increase in crop yield of 1.7-2.3 t/ha. The protectants of the SC series also influenced the quality of the crop, reducing the weight percentage of unsuitable tubers by 2.9-4.4 times and increasing the yield of healthy tubers by 1.4 times. A universal composition for reducing the prevalence of dry rot during storage and development of black scab during the growing season, as well as improving crop productivity and the quality of the products obtained is SC-210.

In order to develop new formulations of protectants on the basis of TBC, the composition with the inclusion of the original fungicide (benomyl) and polysaccharide (kelp), was studied. preparation of suspension forms, kelp was used, which made it possible to obtain stable suspensions and they were tested as disinfectants on potato tubers [15]. The highest biological efficacy (at the level of 50%-57%) against dry rot during storage was shown by protectants No. 1 (TBC/kelp, 1/10) and No. 2 (TBC/kelp/Ca-sulfonol, 1/9/1). The weight percentage of tubers with dry rots during storage during autumn experimental formulations treatment was lower by 1.5-2.3 times in comparison with the control variant, whereas in the variant with chemical standard, this indicator was 3.5-5.6 times higher.

In comparison with the control, all protectants statistical assurance reduced the development of the disease in the period of sprouting by 1.1-7.0 times or the plants were completely healthy, and in the budding-flowering phase 1.5-3.8 times. This indicator in the standard was, respectively, 1.9 times and 3.8 times. Most of all, the development of black scab (up to 3.8 times) during the growing season was reduced the protectants No. 1 and No. (TBC/Benomil/kelp/Ca-sulfonol, 1/1/9/1). Plants, cultivated from treated tubers in autumn, were significantly higher affected by the disease than plants grown from seed treated in the spring before planting (1.2 times in the sprouting phase and 1.9 times in the budding-flowering phase).

The studied suspension protectants had an impact on the biometric parameters of the culture, which contributed to a significant increase in plant height in comparison with the control variant by 2.3-5.6 cm, depending on the phase of the plants. For the standard, this figure was 2.8-9.6 cm. The retardant effect was observed in the studied treaters (plants, grown from tubers treated in the fall were significantly higher by 4.3 cm, than those cultivated from the tubers treated in spring), which smoothed over toward the budding phase. In the late phases of ontogenesis, a significant increase in the mass of potato plants was observed—the weight of one stem was higher by 39.6-130.1 g, than in the control and in the variant with the TMTD, SC 40 (standard).

The gross yield of tubers was increased (up to 10%-42%) by all developed protectants. As a result of comprehensive studies, a No. 1 protectant was proposed as a universal compound for reducing the prevalence of dry rot during storage and development of black scab during the growing season, as well as increasing the productivity of culture and the quality of the products obtained. These data once again confirmed the efficacy of the mechanochemical modification for poorly soluble fungicides using joint mechanical treatment of TBC and kelp.

# 4. Conclusions

According to the results of the research, it can be done the following conclusions:

- To obtain multicomponent protectants, an environmentally friendly mechanochemical method has been proposed. The advantage of the mechanochemical method for the synthesis of supramolecular inclusion complexes is the possibility of obtaining the final product in one technological stage without the use of toxic organic solvents.
- Taking into account some physicochemical properties of the fungicides studied (in particular, low melting point and low solubility in solvents), a mechanochemical suspension technology was proposed using variable-voltage shredders. At the same time, stable suspensions were obtained, which made it possible to effectively dress the potato tubers.
- Biological tests obtained treaters which allowed concluding that universal protectants (in the form of SD and suspensions) to reduce the prevalence of dry rot during storage and development of black scab during the growing season, as well as increasing the productivity of culture and the quality of the products obtained can be obtained as on the basis of No. 2 component systems (based on TBC and TMTD), and multicomponent systems (with the addition of benzimidazole fungicides-BMC, benomyl).

# Acknowledgment

This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

# References

- Ivanyuk, V. G., Banadyshev, S. A., and Zhuromsky, G.
  K. 2005. Protection of Potatoes against Diseases, Pests and Weeds. Minsk: Belprint, 696. (in Russian)
- [2] Zakharenko, V. A. 2015. "Innovative Development of Integrated Management of Phytosanitary Condition of Potato Ecosystems." In Potato Farming: History of Development and Results of Scientific Research on Potato Culture, Moscow, 346-52. (in Russian)
- [3] Kuznetsova, M. A., Rogozhin, A. N., Smetanina, T. I.,

- and Denisenkov, I. A. 2017. "Protection of Potatoes against Rhizoctoniosis, Anthracnose and Silver Scab." *Potatoes and Vegetables* 4: 27-9. (in Russian)
- [4] Melnikov, N. N. 1987. Pesticides Chemistry, Technology and Application. Moscow: Chemistry, 712. (in Russian)
- [5] De Jong, W. I., and Born, P. I. A. 2008. "Drug Delivery and Nanoparticles: Applications and Hazards." *Inter. J. Nanomedicine* 3 (2): 133-49.
- [6] Satish, K. P., Kalpesh, S. W., Venkatesh, B. P., Anup, M. A., and Dheeraj, T. B. 2011. "Strategies for Solubility Enhancement of Poorly Soluble Drugs." *International Journal of Pharmaceutical Sciences Review and Research* 8 (2): 74-80.
- [7] Khalikov, S. S., Dushkin, A. V., Khalikov, M. S., Meteleva, E. S., Evseenko, V. I., Buranbayev, V. S., Fazlaev, R. G., Galimova, V. Z., and Galiulina, A. M. 2011. "Mechanochemical Modification of the Properties of Anthelmintic Drugs." *Chemistry for Sustainable Development* 19 (60): 705-10. (in Russian)
- [8] Khalikov, S. S., Dushkin, A. V., Davletov, R. D., and Evseenko, V. I. 2013. "Creation of Innovative Fungicidal Agents based on Tebuconazole with the Involvement of Mechanochemical Processes." *Basic Research* 10 (12): 2695-700. (in Russian)
- [9] Malyuga, A. A., Chulikova, N. S., and Khalikov, S. S. 2017. "Complex Preparations Based on Carbendazim for Protection of Potato." Advances in Current Natural Sciences 2: 15-20. (in Russian)
- [10] Malyuga, A. A., Chulikova, N. S., and Khalikov, S. S. 2017. "The Carbendazim-Based Complex Preparations for Potato Protection." *Agrochemistry* 6: 52-61. (in Russian)
- [11] Chistyachenko, Y. S., Meteleva, E. S., Pakharukova, M. Y., Katokhin, A. V., Khvostov, M. V., Varlamova, A. I., Glamazdin, I. I., Khalikov, S. S., Polyakov, N. E., Arkhipov, I. A., Tolstikova, T. G., Mordvinov, V. A., Dushkin, A. V., and Lyakhov, N. Z. 2015. "Physicochemical and Pharmacological Study of the Newly Synthesized Complex of Albendazole and Polysaccharide Arabinogalactan from Larch Wood." Current Drug Delivery 12 (5): 477-90. doi: 10.2174/1567201812666150518094739.
- [12] Selyutina, O. Y., Khalikov, S. S., and Polyakov, N. E. 2017. "Comparison of Penetration of the Treater Components by Nuclear Magnetic Resonance Method." Agrochemistry 4: 90-3. (in Russian)
- [13] Khalikov, S. S., Chkanikov, N. D., Spiridonov, Y. Y., and Glinushkin, A. P. 2016. "New Preparation for Presowing Treatment of Seeds with Complex Protection against Diseases and Residues of Herbicides in the Soil." Agrochemistry 6: 39-45. (in Russian)
- [14] Khalikov, S. S., Malyuga, A. A., and Chulikova, N. S.

2018. "Complex Chemicals for Potato Protection Based on Tebuconazole." *Advances in Current Natural Sciences* 2: 55-61. (in Russian)

[15] Khalikov, S. S., Malyuga, A. A., and Chulikova, N. S.

2018. "Ecologically Safe Preparations Based on Mechanochemical Modification of Tebuconazole for Complex Protection of Potatoes." *Agrochemistry* 10: 46-53. (in Russian)