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COMMUNICATION

The Use of Polyvinyl Alcohol's Complexes for Plants Protection Against Diseases and Pests

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ABSTRACT

The research is devoted to elaboration of new materials for agricultural use what is regarded as an urgent need for environment pollution decrease and enhancing of farming efficiency. Gel of polyvinyl alcohol complexed with boric acid or borax is suggested first time as the base of "aroma fixative" for volatile compounds possessing by insect repelling effect. Some new principles are discussed in favor of replacement of common inorganic pesticides like copper compounds on their polymeric complexes. The main positions among them are: 1) formation of biocidal coverings relatively stable at different weather conditions; 2) better adherence of preparations to a surface of protected plant; 3) possibility of biocidal activity mitigation and 4) homogeneity of biocidal coverings. Mitigated biocidal activity is regarded in relation with preparations' influence on plants. An impact on plants and safeguarding behavior against plant diseases and pests were investigated for polyvinyl alcohol's complexes with boric acid and borax, copper hydroxychloride and hydroxide, iron(III) chloride and tar. Their efficiency against spider mite, Colorado beetle and tomato diseases was discovered. It is expected that their use will allow drastic decrease in pesticides' side action, expenses and environmental pollution in agriculture. Thus, the need for the following deeper investigations of above mentioned materials in farming is substantiated.

Keywords: Pesticides; Fungicides; Insecticides; Acaricides; Polyvinyl Alcohol; Colorado Beetle; Spider Mite; Plants Protection

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1. Introduction

The task of plants safeguarding against diseases and pests with minimal expenses and environmental pollution is highly relevant. Hydrogels are considered as convenient carriers for pesticides and fertilizers [1]. One well known antiseptic used also in agriculture is iodine complex with polyvinyl alcohol (PVA) [2]. It possesses milder action in comparison with pure iodine and is not so harmful to animals and plants. PVA also forms complexes with many other compounds [3]. Particularly, PVA-borax complex was suggested as a fertilizer carrier for agricultural applications [4]. The idea of insoluble inorganic substances' biocidic activity mitigation through their complexing with PVA was proposed earlier [5]. Except for milder biological activity, PVA's complexes have other peculiarities important for applications: 1) they form protective coverings that are relatively durable in ambient conditions; 2) they provide good adherence of biocidal covering to the protected object; 3) they possess homogeneous consistency. The latter property allows more effective and sparing resource use, decreasing environmental pollution and mitigation of harm to animals and plants due to the following reasons. Some pristine inorganic biocides like copper hydroxychloride (tribasic copper chloride, TBCC) are insoluble compounds. It is difficult to stick them on the protected surface. Supplemental adhesives are needed which isolate biocide particles and therefore reduce their activity. For the efficiency increase the particle's surface/volume ratio should be enhanced because only surface matters. An active component in homogeneous substance like polymeric complex has maximal possible dispersity. The thickness of the protecting layer can be minimal. These properties provide better efficiency of biocide and minimal environmental pollution. This approach is quite innovative. Earlier, the polymeric films and coverings mainly with the dispersed particles of insoluble inorganic biocides were proposed for the food protection and safeguarding against human infections [6,7]. Contrary to the mentioned insoluble compounds, some other biocides are well-soluble and are washed easily away from plants by rainfall. Polymeric complexes use allows the elimination of this flaw [8].

Organic compounds like alcohols possess biocidic activity as well. Their drawback is high volatility. It can be mitigated using an "aroma fixative" which keeps volatile substances. The author suggests using PVA complexes with boric acid or borax as such fixative. It is accepted that boric compounds in these complexes cross-link PVA's chains [3]. The author believes that low-molecular organic compounds can be captured in the complexes mentioned above. The author also observed a similar but weaker effect for pristine PVA.

Boric acid, borax, iron(III) chloride, tribasic copper chloride (TBCC) and copper(II) carbonate hydroxide were chosen for the investigations as inorganic components of the complexes with PVA. Boric acid and borax are known as relatively weak antiseptics poorly dissolving in water. On the contrary, iron(III) chloride is a substance aggressive to the living being and highly dissolving in water. TBCC is an insoluble in water compound known for its fungicidal activity. Copper(II) carbonate hydroxide does not dissolve in water and is not regarded itself as dangerous for living creatures. But it can be potentially dangerous due to copper containing. All above mentioned compounds are quite cheap available commercial products of bulk chemical production. Preparations with boric acid and borax have similar biocidal activity. The PVA complex with aluminum chloride was also taken into consideration. It was found that its biocidal behavior is similar to that of PVA- iron(III) chloride complex. The interaction of copper(II) carbonate hydroxide with PVA dissolved in water ammonia solution actually is a kind of the production of the known complex of PVA with copper hydroxide.

Birch tar and coal tar (in the form of "Creolin" composition) were also used as the organic additives to the PVA complexes with boric acid and borax. Both are also quite cheap available commercial products of bulk chemical production and contain some low-molecular organic antiseptics like cresols.

The aim of this short communication is to introduce two novel classes of plant-safeguarding preparations with the purpose of conducting further thorough investigation.

2. Materials and Methods

For the formulations preparation the following components were used: 098-15 grade (made in China) polyvinyl alcohol ($-(CH_2\text{-}CHOH)_n-$), "chemical pure" grade sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) (borax),

"technical" grade boric acid ($B(OH)_3$), commercial composition "HOM" (86 % tribasic copper chloride $Cu_2(OH)_3Cl$), "GOST 8927-79" grade (made in Russia) copper(II) carbonate hydroxide ($Cu_2(CO_3)(OH)_2$), "pure" grade iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), commercial compositions "Creolin" (the water dispersion of coal tar, sodium hydroxide and soap), commercial "birch tar" and technical grade ammonium NH_4 water solution. All initial water solutions contained 1 % PVA. Components ratio in the PVA complexes with boron, iron and copper compounds was 3 PVA units (1 unit is $-CH_2$-$CHOH^-$) to 1 atom of boron, iron or copper. According to the earlier investigations (including unpublished results) this ratio corresponds to stoichiometric complexes [9,10]. At higher content of an inorganic component it falls out as separate phase at the solution drying out. Used 1 % (at PVA) solutions of the PVA complexes with boric acid, borax and iron(III) chloride are stable during at least several years according to our observations. Stability of the solutions of the PVA complexes with copper needs further investigation. Copper compounds were dissolved in water ammonia solutions. Ammonia content in the initial solutions was approximately 12 %. Before the use they were 200 times diluted with water.

The solution with the birch tar was prepared by mixing of 30 ml of tar with the 1 l of 1 % (relating to PVA) complex with boric acid or borax. It was preliminary observed that nearly at this ratio tar "dissolves" in complex's solution. At higher tar content it falls out as a separate phase. Solution with the coal tar was prepared by adding 25 ml of commercial Creolin composition into the 1 l of 1 % (relating to PVA) complex with boric acid or borax. Optimization of above-mentioned compounds with birch and coal tars needs additional investigations.

Spraying of all pointed-out plants with the investigated preparations was performed before their excessive moistening. It allows maintaining comparable conditions in a series of experiments. The above-mentioned preparations were used without dilution. Their optimization is regarded as the purpose of further research. Observations were performed with Colorado potato beetles (Leptinotarsa decemlineata) at different life cycle periods (larvae and adult). It is known as a major pest of potato crops resistant to pesticides. Therefore, the development of effective and environment-protecting means against it is an urgent need. The pests were collected in natural conditions, not intentionally bred. Potato leaves remained at the plant during day and night after preparation deposition. After that they were ripped off and placed into the container with the beetles. They were repeatedly replaced every day and night. Such a procedure should imitate, to some extent, field conditions of pesticide use with the aim of better understanding its influence on the pests. In other experiments tree leaves or some separate potato plants with the pests were treated at natural conditions.

The spraying of tomato plants of different kinds with solutions of the PVA complexes with copper compounds was performed repeatedly every 5–10 days four times during the season.

3. Results and Discussion

In our experiments it was found that the treatment of the tomatoes plants with the water solutions of PVA complexes with copper led to the sufficient decrease of spoiled fruits. At the use of the PVA complex with TBCC the ratio of spoiled fruits was 0.5 %. Thirty-four plants were exposed. In the control group of 5 untreated plants, the ratio of spoiled fruits was 16 %. After the treatment of 15 plants with the water solution of the PVA complexes with copper hydroxide, no spoiled fruits were observed. Nearly 100 times sparing of copper compounds was achieved in comparison with the treatment by the traditional means. The positive feedback concerning these preparations was also obtained from other involved farmers.

The potato plants' treatments by the reference preparations – pristine tar or 1.5 % water solution of iron(III) chloride lead to severe damage, the extent of which depends on the kind of the plant. Conversely, the treatment with PVA complexes with the above-mentioned compounds does not lead to such severe damage, though the treatment of the potato leaves with the water solution of PVA complex with iron(III) chloride was quite sensitive for them. The treatment of the plants with the water solutions of PVA complexes with boric acid or borax does not lead to noticeable consequences. For illustration purposes, the photos of the potato leaves before and day and night after the treatment are presented in **Figure 1**. The leaves treated by the water PVA mixture with tar, water solution

of PVA complex with borax and pristine tar are shown there (**Figure 1A** and **1B**).

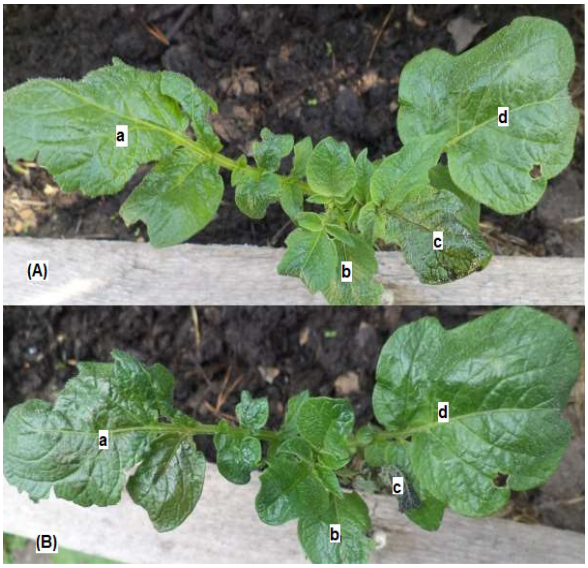

Figure 1. The Potato Leaves Treated with the PVA-Tar Water Solution (*a*), Water Solution of the PVA Complexes with Borax (*b*), Pristine Birch Tar (*c*), and Without Treatment (*d*). **(A)** - Immediately After the Treatment, **(B)** - Day and Night After the Treatment.

The treatment with the water solution of PVA complex with boric acid or borax allows one to get rid of spider mites. To prove this, **Figure 2** shows photos of the cucumber sprouts that suffered from the spider mite before (**Figure 2A**) and some time after dipping them in the water solution of the PVA complex with borax (**Figure 2B** and **2C**).

Figure 2. The Cucumber Sprout Suffered from a Spider Mite Before **(A)**, Two Dais After **(B)** and Three Weeks **(C)** After the Treatment with the 1 % (on PVA) Water Solution of PVA with Borax.

The influence of the water solution of PVA complex with boric acid or borax on larvae was not observed (**Figure 3**). The repelling action was discovered for the PVA complex with boric acid and Creolin (**Figure 4**).

Figure 3. The Leaf with a Colony of Pests Before and Day and Night After the Treatment with 1 % (on PVA) Water Solution of PVA Complex with Borax.

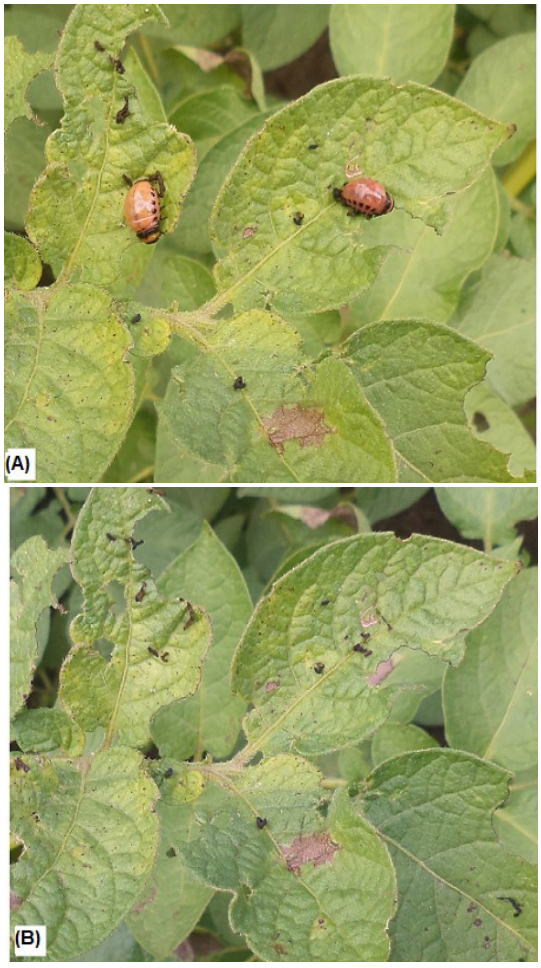

Figure 4. The Potato Leaf with the Colorado Beetle Larvae Immediately After the Treatment **(A)** and 3 Hours After **(B)** the Treatment with Water Solution of PVA Complex with Boric Acid and Creolin.

The distinct specific scent was noticed during nearly 3 days at the potato leaves treated with water solution of PVA complex with boric acid and Creolin (Figure 4A and

4B). The larvae and adult Colorado beetle actively ate fresh untreated potato leaves placed in the container with them. Conversely, they reluctantly ate the potato leaves treated with the PVA complex with iron(III) chloride or PVA complex with boric acid and tar. After that, they perished in 3–4 days.

4. Conclusions

Complexes of polyvinyl alcohol seem to be an efficient means for the protection of plants from diseases and pests. Their use is the first time proposed. In particular, the PVA complexes with copper compounds and boric acid or borax by itself and with tar addition can be recommended for further investigations. Their estimated main advantage is the nearly 100 times decrease of pesticide expenditure.

5. Patents

Prosanov, I.Yu., 2022. Polymeric complex of boron. Patent of Russia. 2774439. 2022 June 21.

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Informed Consent Statement

Not applicable

Data Availability Statement

There are no publicly archived datasets analyzed or generated during the study.

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Conflicts of Interest

The author declares no conflict of interest.

References

[1] Malka, E., Margel, S., 2023. Engineering of PVA/PVP Hydrogels for Agricultural Applications. Gels. 9(11), 895–895. DOI: https://doi.org/10.3390/gels9110895

[2] Makhayeva, D.N., Irmukhametova, G.S., Khutoryanskiy, V.V., 2023. Advances in antimicrobial polymeric iodophors. European Polymer Journal. 201, 112573. DOI: https://doi.org/10.1016/j.eurpolymj.2023.112573

[3] Finch, C.A., 1983. Some properties of polyvinyl alcohol and their possible applications. In: Finch, C.A. (ed.). Chemistry and technology of water-soluble polymers. Springer Science+Business Media: New York, USA. pp. 287–306.

[4] Kale, S.N., Mona, J., Dhobale, S., et al., 2011. Intramolecular and Intermolecular Crosslinked Poly(vinylalcohol)–Borate Complexes for the Sustained Release of Fertilizers and Enzymes. Journal of Applied Polymer Science. 121(4), 2450–2457.

[5] Prosanov, I.Yu., 2022. Innovation materials for biocidal coverings production [in Russian]. Science and Technology of Siberia [in Russian]. 5, 33–34.

[6] Abedi-Firoozjah, R., Chabook, N., Rostami, O., et al., 2023. PVA/starch films: An updated review of their preparation, characterization, and diverse applications in the food industry. Polymer Testing. 118, 107903. DOI: https://doi.org/10.1016/j.polymertesting.2022.107903

[7] Jabbar, G.A.H.A., Saeed, A.A., Al-Kadhemy, M.F.H., 2023. Optical characteristics and bacterial-resistance ability of PVA/ZnO nanocomposites. Kuwait Journal of Science. 50(3), 209–215. DOI: https://doi.org/10.1016/j.kjs.2023.03.004

[8] Hay, W.T., Behle, R.W., Ruiz-Ver, U.M., et al., 2020. Use of novel film forming starch complexes to directly and indirectly reduce insect damage to plants. Crop Protection. 130, 105048. DOI: https://doi.org/10.1016/j.cropro.2019.105048

[9] Prosanov, I.Yu., 2022. Polymeric complex of boron. Russian Patent. 2774439. 2022 June 21.

[10] Prosanov, I.Yu., Benassi, E., Bulina, N.V., et al., 2018. Polymeric Copper Oxide: Preparation and Investigation of Its Structure and Optical Properties. Journal of Inorganic and Organometallic Polymers and Materials. 28(6), 2328–2335. DOI: https://doi.org/10.1007/s10904-018-0897-5