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ORIGINAL ARTICLE

RESULTS OF RESEARCH OF PERSONAL HYGIENE PRODUCTS FOR SUITABILITY FOR SPECIAL PROCESSING IN ZONES OF CHEMICAL, RADIOACTIVE CONTAMINATION AND IN COMBAT CONDITIONS

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ABSTRACT

The aim: Research of personal hygiene products with detoxification properties by evaluating their formulation composition, emulsifying and complexing ability to heavy metal ions and radionuclides.

Materials and methods: The complex-forming ability of raw materials with heavy metal ions was determined in vitro, the content of heavy metals was determined by the method of atomic emission spectrometry with inductively coupled plasma (BS EN 13805:2014); determined the content of ¹³⁷Cs, ²³²Th, ⁴⁰K, ²²⁶Ra, ⁹⁰Sr in washings from the surface of the skin of hands treated with personal hygiene products. The means were tested for compliance with the standard on scintillation spectrometers of gamma radiation energy «SEG-001» «AKP-S» and beta radiation (SEB-01-70); methods used: MI 12-04-099 and MI 12-05-099.

Results: A high complexing ability of the pectin-containing «Liana» shampoo was found in relation to heavy metal ions (Co²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺), as well as in their combined presence. It was established that the effectiveness of removing fatty impurities from the surface of the skin of the «Liana» product was 10.1 times higher than that of liquid soap (p<0.001). A high level of deactivating, degassing and antibacterial properties of the personal care products «Bastion» and «Bastion-M» was revealed.

Conclusions: Today, there is significant potential in the creation of formulations for special (sanitary) skin and hair surface treatment, containing natural complexing agents as detoxicants, and can be used in special professional activities associated with the risk of exposure to CBRN factors.

KEY WORDS: special treatment, sanitary treatment, heavy metals, radionuclides

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INTRODUCTION

In the conditions of increasing endogenous and exogenous pollution of the environment, which is a consequence of the Chernobyl disaster, hostilities, inundations caused by floods and other disasters, special processing of the terrain, defense structures, weapons, equipment, uniforms, shoes, personal protective equipment become important, medical and sanitary property, personnel and places of temporary residence and mass stay of the population [1-4]. A component of special processing is degassing, detoxification and disinfection. Special processing consists in removing radioactive substances, chemical and biological agents from the uniforms and skin of personnel of military units [5]. An element of special processing is sanitary processing.

The analysis of scientific research in the field of special treatment products has shown that promising products for the sanitary treatment of skin and hair are deactivating shampoos for hair and body and personal hygiene with deactivating, degassing and antibacterial action, which,

thanks to their balanced composition, are detoxifiers for external use and have deactivating, degassing and antibacterial properties and can be used as intended in hazardous conditions in the CBRN.

THE AIM

Study of suitability for use in CBRN contamination zones and combat conditions of personal hygiene products with deactivating, degassing, detoxification properties by evaluating their formulation composition, emulsifying and complexing ability in relation to heavy metal ions, and ability to remove radionuclides from skin and hair surfaces.

MATERIALS AND METHODS

The complex-forming ability of pectin (raw material), shampoo and hygiene products (Liana, Bastion, Bastion-M) in relation to heavy metal ions was found in vitro. The effectiveness

Table I. Complexing ability of pectin solution in relation to heavy metal ions

| Object of study | Complexing ability of pectin, mg met/g pectin | | | | |
|-----------------|---|------------------|------------------|------------------|------------------|
| | Co ²⁺ | Cu ²⁺ | Zn ²⁺ | Cd ²⁺ | Pb ²⁺ |
| Apple pectin | 260 | 203 | 200 | 195 | 254 |

*The presence of globules is observed.

Table II. Complexing ability of pectin-containing shampoo «Liana» in relation to heavy metal ions in their combined presence

| Object of study | Complexing ability, % | | | | |
|--|-----------------------|------------------|------------------|------------------|------------------|
| | Co ²⁺ | Cu ²⁺ | Zn ²⁺ | Cd ²⁺ | Pb ²⁺ |
| Pectin-containing deactivating shampoo «Liana» | 25 | 20 | 18 | 15 | 22 |

*The presence of globules was observed. The presence of sediment in the form of globules indicates pectin/metal complexation.

Table III. Complexing ability of shampoo – control No. 1 in relation to heavy metal ions in their combined presence

| Object of study | Complexing ability, % | | | | |
|---------------------|-----------------------|------------------|------------------|------------------|------------------|
| | Co ²⁺ | Cu ²⁺ | Zn ²⁺ | Cd ²⁺ | Pb ²⁺ |
| Shampoo – control * | 0,9 | 1,1 | 0,2 | 0,02 | 4,2 |

* Absence of globules was observed, there is a small sediment.

Table IV. Complexing ability of shampoo – control No. 2 in relation to heavy metal ions in their combined presence

| Object of study | Complexing ability, % | | | | |
|---------------------|-----------------------|------------------|------------------|------------------|------------------|
| | Co ²⁺ | Cu ²⁺ | Zn ²⁺ | Cd ²⁺ | Pb ²⁺ |
| Shampoo – control * | 0,8 | 0,2 | 0,02 | 0,01 | 0,5 |

* Absence of globules was observed, there is a small sediment.

of removing heavy metal ions from the surface of the skin was determined in washings from the hands of employees of JSC «State Joint-Stock Company «Automobile Roads of Ukraine» of the subsidiary «KhmelnyskiyOblavtodor» branch of «Rusanivnisky Special Quarry». Determination of the content of heavy metals was carried out by the method of atomic emission spectrometry with inductively coupled plasma (sample preparation according to BS EN 13805:2014) [6]. Washes from the surface of the skin of hands treated with hygiene products were examined for the content of ¹³⁷Cs, ²³²Th, ⁴⁰K, ²²⁶Ra, ⁹⁰Sr (Basic sanitary rules for ensuring radiation safety of Ukraine, 2005, DSP 6.177-2005-09-02.). Determination of radionuclide content was performed on scintillation energy spectrometers of gamma radiation (SEG-001 «AKP-S») and beta radiation (SEB-01-70) [7, 8]. Measurements were carried out according to the MI 12-04-099 method using the SEG-002 «AKP-P» semiconductor type gamma radiation energy spectrophotometer and the MI 12-05-099 method using the SEB-01 scintillation type beta radiation energy spectrophotometer. The relative measurement error ranges from ±10% to ±50% at p < 0.05. Pectin was used (brand SWEJ-1 manufactured by PEKTOWIN Sp.zo.o.), obtained from apple pomace by acid-thermal hydrolysis of raw materials.

RESULTS

It is known that products containing pectins are effective detoxification, as studies have shown. Pectins, due to their gel- and structure-forming properties and the ability to

bind heavy metal ions, have shown themselves well as hygienic preventive means for removing heavy metal salts and radionuclides from skin and hair surfaces. Salts of heavy metals, primarily lead, zinc and oil, are quite widely available in the metalworking, glass, textile, porcelain and earthenware and other industries, as well as as a result of hostilities, where there is catastrophic damage to the environment by factors of various origins, harmful effects on which. human health largely depends on solubility in water and fats, duration and ways of entering the body. It is indisputable that the creation of external detoxification agents, which creates natural complexing agents of plant origin, is an actual direction in the field of cosmetics, food industry, and medicine and should have a scientific basis.

As part of the research work, some characteristics of the deactivating shampoo for hair and body «Liana» were studied. «Liana» was manufactured in accordance with technical requirements: U 24.5-2859920992-001:2006 «Shampoos for hair and body with deactivating properties. Technical conditions» for use as a personal hygiene product for workers in heavy metallurgy, nuclear power plants, mining and chemical industry; everyday life (including for use in emergency situations). Manufacturer: Ukrainian-Bulgarian LLC «Pirana» (Kharkov), by order and according to the technology of IE «Shokur A.A.» and packaged by «BARA» LLC.

On the basis of the L.I. Medved's Research center of preventive toxicology, food and chemical safety of the Ministry of Health of Ukraine studies were conducted on the complexing

Table V. Test results of deactivating shampoo for hair and body «Liana» according to physical and chemical indicators

| Indicator name | Requirements for documentation | Actual value | The unit of measurement | Regulatory requirements for research methods | The relative error of the tests |
|--|--------------------------------|--------------|-------------------------|--|---------------------------------|
| Kinematic viscosity at a temperature of 20°C | - | 698 | mm ² | State Standard GOST 33 | 0,35 %** |

**The permissible relative difference between two consecutive determinations should not exceed the given value.

Table VI. Results of studies of model environments No.1 (combined sample)

| Indicator | Actual value, mg/dm ³ | Regulatory requirements for research methods |
|-----------|----------------------------------|--|
| Lead | 0,602 | State Standard GOST 30178-96 |
| Cadmium | not revealed | |
| Copper | 2,806 | |

Table VII. Results of studies of model environments No. 2 (combined sample)

| Indicator | Actual value, mg/dm ³ | Regulatory requirements for research methods |
|-----------|----------------------------------|--|
| Lead | 0,010 | State Standard GOST 30178-96 |
| Cadmium | not revealed | |
| Copper | 0,050 | |

ability of apple pectin, pectin-containing shampoo «Liana», control shampoos No.1 and No.2 (which contained all components of the pectin-containing deactivating shampoo formulation, except for pectin), with heavy metal ions. Heavy metal ions were determined in washings by atomic absorption method (tables I-IV).

A test of the emulsifying ability of a pectin-containing shampoo in relation to fatty impurities was carried out. The pectin-containing deactivating shampoo «Liana» was 10.1 times ($p < 0.001$) higher than this indicator for liquid soap in terms of its effectiveness in removing fatty impurities from the surface of the skin.

The product was checked for microbiological safety indicators, the mass fraction of surfactant (according to the stated method for determining – Standard SEB 2542), kinematic viscosity at a temperature of 20°C (table 5), as well as washes from the surface of hands treated with pectin-containing deactivating shampoo for hair and body «Liana», and washed from the surface of hands treated with liquid soap, according to radiological indicators (Table V).

The obtained data indicate that with the available mass fraction of surfactant and given kinematic viscosity, uniform application of the product to the skin and its subsequent washing off are ensured. Radiological studies have shown that deactivating shampoo for hair and body «Liana» has the ability to remove radionuclides from the surface of the skin, namely: ¹³⁷Cs 1.06 times, ²³²Th by 1.12 times, ⁴⁰K by 26.19 times and ⁹⁰Sr by 2.52 times more effective than liquid soap ($p < 0.001$).

In cooperation with «Shokur A.A.» LLC additional studies were carried out at the Institute of Geochemistry, Mineralogy and Ore Formation them. M.P. Semenenko, National Academy of Sciences of Ukraine (an act of research on the complex-forming ability of pectin with respect to heavy metals, the pectin-containing deactivating shampoo «Liana», control

shampoos No.1 and No.2, which contained all components of the pectin-containing deactivating shampoo recipe, except for pectin, and the effectiveness of the pectin-containing deactivating shampoo «Liana». The obtained results confirmed the effectiveness of the «Liana» shampoo in removing heavy metal ions.

Therefore, according to the results of review of accompanying documents (test reports of shampoo for hair and body with deactivating properties «Liana», issued by SE «Khmelnitskyi Regional Center for Standardization, Metrology and Certification» and protocol of radiological control of products issued by DU «Khmelnitskyi Regional Laboratory Center of the Ministry of Health of Ukraine»), risk assessments for public health, namely (no more, in points): skin irritation index – 0; acute toxicity index when applied to the skin – 0; index of chronic toxicity when applied to the skin – 0; index of irritating action on the mucous membrane of the eyes – 2; acute toxicity index when administered into the stomach – 1; index of sensitizing effect – 0; bacteria genus Enterobacteriaceae, in 1 cubic cm – are not allowed; S. aureus, in 1 cm³ – are not allowed; Pseudomonas aeruginosa in 1 cubic cm – are not allowed; yeast and mold fungi, CFU/g – no more than 100; the total number of MAFAM, CFU/g – no more than 1000; hydrogen index – within 3.5-8.5 units. pH, mass fraction of surface-active substances – no more than 15.0% and the efficiency tests of the product, deactivating shampoo for hair and body «Liana» meets the requirements of «State sanitary rules and safety standards of products of the perfumery and cosmetics industry – standards: DSanPiN 2.2.9.027-99 and TU 24.5-2859920992-001:2006, and can also be used in the declared field: «Personal hygiene product for workers in heavy metallurgy, nuclear power plants, mining and chemical industry; daily life (including for use in emergency situations)».

A study of the effectiveness of removing heavy metal ions from the skin of employees of OJSC "State Joint Stock Company "Automobile Dorogy of Ukraine" of the subsidiary "Khmelnyskyi Oblavtodor" of the branch "Rusanivnyskyi Special Quarry" showed that "Liana" shampoo was able to remove lead from the surface of the skin in 60, 2 times, copper is 56.12 times more effective than liquid soap. In addition, washings of dirt from the surface of the skin treated with liquid soap contained more non-emulsified fatty phase than washings of dirt from the surface of skin treated with pectin-containing deactivating shampoo for hair and body "Liana", while, according to the observations of the doctor of the sanitary department of the branch, the condition of the skin was determined as unsatisfactory, as the presence of fuel oil residues and other organic and inorganic contaminants was visually recorded in the pores of the skin.

The washes of dirt from the surface of the skin treated with pectin-containing deactivating shampoo "Liana" (model environment No.1) and the washes of dirt from the surface of the skin treated with liquid soap (model environment No.2) are presented in the tables VI-VII.

Personal hygiene product «Bastion» produced by «Energochem Scientific and Production Association» LLC was tested for compliance with domestic legislation and technical conditions of U 20.4-31454306-014:2014 «Bastion personal hygiene products (deactivating, degassing, antibacterial, detoxifying). Studies on determining the complex-forming ability in relation to heavy metal ions and radionuclides of the personal care product «Bastion» revealed that the product not only has a high complex-forming ability in relation to heavy metals, but also prevents contamination of the skin by microorganisms from the yeast family (*Malassezia furfur* and *Pityrosporum oval*).

DISCUSSION

The obtained data demonstrate that the means «Bastion» and «Bastion M» are expedient to use not only in production conditions associated with the use of salts of heavy metals and radioactive metals, but also as a dermatological protective agent for daily cleaning and protection of the skin and its appendages from exogenous pollution. The experimentally established effective amount of the products for the body and its appendages is calculated from 15 cm³ to 20 cm³: contact time with the surface of the skin (exposure) of the body and its appendages is 2 minutes, taking into account the application and uniform distribution of the means on the treated body surface.

Previous studies of personal hygiene products containing pectin allow us to conclude that pectin improves the functional state of the epidermis *in vitro* and the physical state of hair, neutralizes the harmful effects of surface-active substances, prevents the disorganization of lipids in the stratum corneum of the skin and the loss of transepidermal moisture. The studies of low- and high-esterified pectins mainly relate to various aspects of their use in the production of food products [9, 10], however, data on the effectiveness of pectins in the composition of hygiene products (shampoos)

are practically absent. Based on the results of our research, we received a Ukrainian patent for the invention [11].

Given that an important and rather complex aspect of special treatment is the sanitary treatment of skin and hair, it is advisable to increase the availability of the above means for use by rescue and military units, as well as their use along with skin disinfection means, which can be solved, for example, by developing kits from disinfectants and personal hygiene products with deactivating, degassing, detoxifying and/or antibacterial properties (according to State classifier of products and services: code 20.2 and code 20.4).

CONCLUSIONS

In conditions of high risk of radioactive, chemical and biological contamination of the human environment, there is a high need for sanitary treatment products that have deactivating, degassing and detoxifying properties due to the content of safe and effective detoxification-complexing agents of plant and/or chemical origin in the formulation. In peacetime or outside the combat zone, individual sets of such tools together with disinfectants were useful for use by the population in everyday life and agriculture (on farms, vineyards, etc.), in the Chernobyl zone and other areas of potential CBRN contamination.

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(state registration number – 0112U001133).

The research was conducted without the participation of humans and animals. The Research Program considers the requirements of the European Convention on European Convention for the Protection of Vertebrate Animals used for Experimental and other Scientific Purposes (1986, Strasbourg) and the legislation of Ukraine in this area; the Research Program was approved by the Bioethics Committee of L.I. Medved's Research Center of Preventive Toxicology, Food and Chemical Safety of the Ministry of Health of Ukraine» (SE).

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Conflict of interest:

The Authors declare no conflict of interest.

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