11TH INTERNATIONAL SCIENTIFIC CONFERENCE ON DEFENSIVE TECHNOLOGIES
OTEH 2024
Serbia, Tara, 9-11 October 2024

IMPACT OF ACTIVE FILLER COMPOSITION MODIFICATION ON THE SORPTION CHARACTERISTICS OF FILTERS

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Abstract: *To expand the protection range of filters against industrial chemical agents, with a focus on carbon monoxide, beyond the protection offered by the existing M3 and CBRN filters, a new alternative filter, named CO CBRN ESC Filter, was developed with a modified active filler composition. In accordance with defined requirements and existing equipment, the laboratory testing was conducted to evaluate the effect of the modified active filler composition in the CO CBRN ESC Filter on the sorption characteristics, specifically regarding protection against NBC agents and industrial toxic chemicals. The CO CBRN ESC Filter contains a dual-component active filler, consisting of a layer of activated carbon impregnated with calcium chloride salts and a layer of hopcalite, which is a mixture of copper and manganese oxides.*

Keywords: *alternative CO CBRN ESC Filter, dual-component active filler, physical-mechanical testing, sorption characteristics of filters.*

1. INTRODUCTION

The onset of the 21st century, marked by terrorist attacks and other forms of threats, has highlighted the need for the protection of both civilian populations and defense personnel. The impact of toxic chemical agents in the form of gases, vapors, and liquid and solid aerosols, which may be employed in such situations but are not classified as warfare agents, often leads to systemic paralysis and unintended consequences. These toxic chemical agents are typically easily accessible and simple to deploy[1], [2]

The need for respiratory protection devices, particularly filters, imposes new and additional requirements for their development. In response to emerging global trends, TRAYAL Corporation, in collaboration with experts from the Military Technical Institute, developed an alternative filter to expand the protection range against various industrial toxic chemicals, with a focus on carbon monoxide. The results of the testing of this alternative filter, referred to as the CO CBRN ESC (hereinafter referred to as the alternative filter), provided a basis for its justified application in various situations. The test gases used to examine the alternative filter included representatives of NBC toxic agents (phosgene, chloropicrin, and hydrogen cyanide), supplemented by gases representative of industrial toxic chemicals (sulfur dioxide, cyclohexane, ammonia, and carbon monoxide). The filters were tested in a laboratory under precisely defined and controlled parameters, including the input concentration and flow rate of the test gas, as well as the humidity and temperature of the air and test gas mixture, which partly correspond to conditions in accidental situations. Accidental conditions imply the potential presence of unforeseen toxic chemical agents, as well as faster movement of the user and accelerated breathing due to fear and panic. Therefore, it is necessary to conduct comparative tests of the alternative filters by modifying one testing parameter, such as only the airflow, to gain a clearer understanding of the filter's applicability in emergency situations.

Previous studies have presented the impact of changing the impregnation of activated carbon as the active filler in M3 Filters, as well as the effect of the height of the active filler on the sorption characteristics of M3 and CBRN Filters under defined testing parameters. The results obtained from these studies provided a good starting point for establishing new protection requirements for the alternative filter against carbon monoxide, to which the tested M3 and CBRN Filters did not respond, alongside the spectrum of other test gases for which the M3 and CBRN Filters met the established criteria. Additionally, the alternative filter can be used with a protective mask

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DOI: 10.5937/OTEH24114M

(both half and full-face masks) as well as with an evacuation hood employed in emergency situations (e.g., fires). [2]
Given the decades-long tradition of producing carbon monoxide (CO) filters at TRAYAL Corporation, the challenge of developing this alternative filter was well-founded. The alternative filter analyzed in this study shares similarities with previous generations of filters, where a dual-component filler (impregnated activated carbon and hopcalite) [4] was used as the active filler. The alternative filter must also meet requirements concerning filter weight limitation (up to 330 g) and inhalation resistance, making it easily applicable for potential users, such as when wearing an evacuation hood or as a filter for children's masks and other masks and half masks.
The CO CBRN ESC Filter contains a dual-component active filler, comprising a layer of activated carbon impregnated with calcium chloride salts [3] and a layer of hopcalite, which is a mixture of copper and manganese oxides [4]. The activated carbon in the alternative filter is produced using TRAYAL Corporation's manufacturing technology, with granulation corresponding to that of the M3 filter's active filler. The activated carbon has an activity level, defined by an iodine number, of no less than 1250 mg/g of activated carbon. Hopcalite, the second component of the alternative filter's active filler, is a material already used at TRAYAL Corporation and consists of a mixture of copper and manganese oxides. The hopcalite is sourced from a long-standing supplier, with the homologation of the mixture performed at TRAYAL Corporation.
The alternative filters used for sorption testing with the test gases were filled with the aforementioned dual-component filler and manufactured according to the standard technology used for M3 Filters. Besides modifications in the active filler, these filters also feature a modified anti-aerosol insert to more effectively utilize the designed space for the active filler.

2. EXPERIMENTAL PART

The examination of sorption properties of the CO CBRN ESC filter was conducted in accordance with the SORS 8748 and SRPS EN 14387 standards.

2.1. Methods for Testing Sorption Characteristics of the CO CBRN ESC Filter against NBC Test Gases (Phosgene, Chloropicrin, and Hydrogen Cyanide)

The methods for testing involve monitoring and recording the protection time as an indicator of the filter's sorption properties when exposed to test gases (phosgene, chloropicrin, and hydrogen cyanide) under defined conditions and testing parameters. These methods include maintaining constant input concentrations of test gases and the relative humidity of the test gas-air mixture while varying the flow rate of the incoming gas mixture. The testing method for sorption characteristics of the CO CBRN ESC filter against NBC test gases phosgene, chloropicrin, and hydrogen cyanide is conducted in accordance with the SORS 8748 standard.
The flow rate of the air and test gas mixture (phosgene, chloropicrin, and hydrogen cyanide) is adjusted until the defined input concentration for the specific test gas and the relative humidity of the gas mixture are achieved. This process is repeated when varying the flow rate of the incoming gas mixture for a specific test gas. The time is measured from the moment the air and test gas mixture enter the filter until the indicator paper changes color. The measured time indicates the protection time of the filter against the specific test gas. [5]

2.2. Methods for Testing Sorption Characteristics against the Effects of Industrial Toxic Test Gases (Sulfur Dioxide, Cyclohexane, Ammonia, and Carbon Monoxide)

The testing methods involve monitoring and recording the protection time as an indicator of the filter's sorption properties when exposed to test gases (sulfur dioxide, cyclohexane, ammonia, and carbon monoxide) under defined testing conditions and parameters. This includes maintaining constant input concentrations of test gases and the relative humidity of the gas-air mixture while varying the flow rate of the incoming gas mixture.
The method for testing sorption characteristics against the effects of sulfur dioxide and ammonia is conducted in accordance with the SRPS EN 14387 standard, while the testing of sorption characteristics against the effects of cyclohexane and carbon monoxide is carried out according to the manufacturer's internal method. [6]

2.2.1. Procedure for testing sorption characteristics method against the effects of sulfur dioxide and ammonia

The flow rate of the air and test gas mixture (sulfur dioxide, cyclohexane, and ammonia) is adjusted until the defined input concentration for the specific test gas and the relative humidity of the gas mixture are achieved. This process is repeated when varying the flow rate of the incoming gas mixture for the specific test gas. The time is measured from the moment the air and test gas mixture enters the filter until the indicator paper changes color. The measured time indicates the protection time of the filter against the specific test gas.

2.2.2. Procedure of the Testing Method for Sorption Characteristics of the CO CBRN ESC Filter against Carbon Monoxide

The gas analyzer and artificial lungs are activated, and the flow rate of the air and carbon monoxide gas mixture is adjusted until the defined input concentration, relative humidity and temperature of the gas mixture in the detection system are achieved. The time is measured from the moment the gas mixture is introduced into the test filter until the gas analyzer detects an output concentration of carbon monoxide test gas in the system at 200 ppm

. 2.2.3. Procedure of the Testing Method for Sorption Time Characteristics of the CO CBRN ESC Filter against Cyclohexane

The flow rate of the air and cyclohexane gas mixture is adjusted until the required input concentration of the test gas and the relative humidity of the gas mixture in the detection system are achieved. The time is measured from the moment the cyclohexane and air gas mixture is introduced into the test filter until an output concentration of cyclohexane at 10 ppm is detected in the system.

3. RESULTS AND DISCUSSION

The CO CBRN ESC filter contains a dual-component active filling, consisting of a layer of activated carbon impregnated with calcium chloride salts, as well as a layer of hopcalite, which is a mixture of copper and manganese oxides (Cu^{2+} and Mn^{4+}). The activated carbon in the alternative filter is produced using the technology developed by TRAYAL Corporation, while the hopcalite is purchased from a long-term supplier and homologated immediately before filling the filter.

3.1. Testing Results of the Physical-Mechanical Characteristics for Both Layers of Active Filling and the Filter

To gain a more comprehensive understanding of the potential broader application and enhanced functionality of the alternative filter, it is necessary to test the following physical-mechanical characteristics for both layers of active filling, in accordance with the SORS 8830/05 standard: moisture content, bulk density, mechanical strength, and granulometric composition. [8] The testing results of the characteristics of the active fillings are presented in Table 1.

Table1. Physical-mechanical characteristics for both layers of active filling in the CO CBRN ESC filter

ACTIVE FILLINGS	Activated Impregnated $CaCl_2$	Hopcalite
MOISTURE CONTENT [%]	1.1	0.48
Bulk Density [G/L]	520.9	785.0
MECHANICAL STRENGTH [%]	78	63
GRANULOMETRIC COMPOSITION (%)		
>1.8 MM	0.00%	3.16%
> 1.6 MM	0.41%	21.19%
>1.4 MM	6.03%	20.04%
0.7-1.4 MM	92.66%	54.91%
	0.89%	0.61%
	0.01%	0.09%

Furthermore, for the alternative filter to be easily applicable when wearing a mask or evacuation hood, it must meet defined requirements regarding the filter's mass (up to 330 g) and inhalation resistance. For these reasons, before testing the filter's sorption characteristics, it is necessary to examine the following physical-mechanical characteristics of the CO CBRN ESC filter in accordance with SORS 8829 and SRPS EN 14387 standards: mass, inhalation resistance, and filtration efficiency using paraffin aerosol mist. The testing results of the CO CBRN ESC filter's characteristics are presented in Table 2.

Table 2. Physical-mechanical characteristics for both layers of active filling in the CO CBRN ESC filter

Filter Type	Mass [g]	Отпор филтера (Pa)	Ефикасност филтрирања (%)
CO CBRN ESC	315	110	1x10^{-3}
COCBRN ESC	330	120	1x10^{3}
COCBRN ESC	327	113	1x10^{3}

The obtained test results presented in Table 1 meet all the requirements related to the physical-mechanical characteristics of the active layers in the filter, while the results in Table 2 satisfy all the requirements for the physical-mechanical characteristics of the CO CBRN ESC filter. This fact is significant not only because it fulfills the necessary requirements but also as confirmation that the manufacturing technology for the alternative filter is justified in terms of functionality and protection, providing a solid basis for the potential application of this filter. Additionally, these preliminary tests are a prerequisite for evaluating the possibility of expanding the protection range of the alternative filter, particularly its use in emergency situations, by testing the filter's sorption characteristics against NBC toxic gases, as well as industrial toxic gases, with a focus on carbon monoxide.

3.2. Testing Results of the Sorption Characteristics of the CO CBRN ESC Filter against NBC Test Gases (Phosgene, Chloropicrin, and Hydrogen Cyanide)

The testing of the sorption characteristics of the CO CBRN ESC filter against NBC test gases (phosgene, hydrogen cyanide, and chloropicrin), expressed as protection time (minutes), was conducted under the following conditions:

- Input concentration of the test gas (phosgene and hydrogen cyanide): 1000 ppm,
- Input concentration of the test gas (chloropicrin): 2200 ppm,
- Relative humidity of the air-gas mixture (phosgene, hydrogen cyanide, and chloropicrin): 80%, and
- flow rate of the air-gas mixture (phosgene, hydrogen cyanide, and chloropicrin): 30 l/min and 64 l/min.

The values of the tested input concentrations of the test gases (phosgene, hydrogen cyanide, and chloropicrin), as well as the humidity of the input test gas-air mixture, were kept constant for all the tested filters. To simulate conditions closer to those encountered during the use of filters in accidental situations, we tested the sorption characteristics of the filters at different gas mixture flow rates of 30 l/min and 64 l/min. [7],[6], [9]

The obtained testing results of the sorption characteristics of the CO CBRN ESC filter against NBC test gases (phosgene, hydrogen cyanide, and chloropicrin), expressed as protection time (minutes), are presented in Table 3 (relative humidity of the gas-air mixture is 80 %).

Table3. Sorption Characteristics of the Filter Against NBC Test Gases (Phosgene, Hydrogen Cyanide, and Chloropicrin)

Test gas	Input concentration [ppm]	Protection time [min] 30 l/min	Protection time [min] 64 l/min
Phosgene	1000	25 23 24	11 10 9
Chloropicrin	2200	36 37 34	29 30 28
Hydrogen cyanide	1000	29 27 30	14 12 12

3.3. Testing Results of the Sorption Characteristics of the CO CBRN ESC Filter against Industrial Toxic Test Gases (Sulfur Dioxide, Cyclohexane, Ammonia and Carbon Monoxide)

The testing of the sorption characteristics of the CO CBRN ESC filter against industrial toxic test gases (sulfur dioxide, cyclohexane, ammonia), expressed as protection time (minutes), was conducted under the following conditions:

- Input concentration of the test gas (sulfur dioxide, cyclohexane, ammonia): 1000 ppm
- Relative humidity of the air-gas mixture (sulfur dioxide, cyclohexane, ammonia): 70% until breakthrough,
- Flow rate of the air-gas mixture (sulfur dioxide, cyclohexane, ammonia): 30 l/min and 64 l/min.

The testing of the sorption characteristics of the CO CBRN ESC filter against the industrial toxic test gas (carbon monoxide), expressed as protection time (minutes), was conducted under the following conditions:

- Input concentration of the test gas (carbon monoxide): 2500 ppm,
- Relative humidity of the air-gas mixture (carbon monoxide): 80% until the breakthrough concentration of 200 ppm, temperature 50 ºC, and
- Flow rate of the air-gas mixture (carbon monoxide): 30 l/min and 45 l/min.

Due to the characteristics of the testing apparatus for evaluating the sorption characteristics of the filter against carbon monoxide, it was not possible to set a flow rate of 64 l/min. The apparatus uses artificial lungs with a working rate of 20 cycles per minute (1.5 l per cycle). The maximum setting allowed by the apparatus is 30 cycles per minute (1.5 l per cycle), or 45 l/min.

The obtained testing results of the sorption characteristics of the CO CBRN ESC filter against these gases (sulfur dioxide, cyclohexane, ammonia and carbon monoxide), expressed as protection time (minutes), are presented in Table 4.

Table4. Sorption characteristics of the filter against industrial test gases (sulfur dioxide, cyclohexane, ammonia and carbon monoxide)

Test gas / Input concentration [ppm]	Relative humidity [%]	Protection time [min] 30 l/min	Protection time [min] 64/ 45* l/min
Sulfur dioxide 1000	**70**	28 30 24	10 9 10
Ammonia 1000	**70**	108 107 112	38 39 39
Cyclohexane 1000	**70**	68 67 66	34.6 29.1 30
Carbon monoxide* 2500	**80**	36 35 39	7 8 8.3

Given that the tests revealed that the new filter does not meet the protection time requirements (15 minutes) for higher flow rates of test gases, specifically against certain NBC gases (phosgene and hydrogen cyanide) and industrial gases (carbon monoxide and sulfur dioxide), filters with a new ratio of activated carbon to hopcalite layers (favoring hopcalite) were produced. Additional testing of the sorption characteristics of the new filters against industrial gases was conducted, and the results are presented in Table 5.

Table 5. Sorption characteristics of the filter (from a new batch) against industrial test gases (sulfur dioxide, cyclohexane, ammonia and carbon monoxide)

Test gas / Input concentration [ppm]	Relative humidity [%]	Protection time [min] 30 l/min	Protection time [min] 64/ 45* l/min
Sulfur dioxide 1000	**70**	46 51 45	14 12
Ammonia 1000	**70**	110 109 113	38 39
Cyclohexane 1000	**70**	48 51.4 49	20 20.4 21
Carbon monoxide* 2500	**80**	43 39 46	8 10 9.3

4. CONCLUSION

The aim of this study is to extend the protection range of the filter to include both NBC agents and industrial toxic gases, as prescribed by the SRPS EN 403 standard. TRAYAL Corporation has developed a filter under the working name CO CBRN ESC, which differs from the M3 and CBRN standard filters in the composition of its active filling. The active filling consists of two distinct components: a layer of activated carbon impregnated with calcium chloride and a layer of hopcalite, with a standard filling height. Accordingly, the influence of the active

filling composition on the sorption characteristics of the filter against NBC agents and industrial toxic gases was examined. To simulate conditions similar to those in accidental situations, the flow rate of the gas mixture was varied, while parameters such as the relative humidity of the gas mixture and the input concentration of the test gas remained constant and were defined by the standard.
Additionally, to meet the functional requirements of this filter and its application as a component of military masks, half-masks, children's protective masks, and evacuation hoods, the testing results for the overall mass of the filter and inhalation resistance have shown that the filter meets the specified requirements.

The testing results indicated that the alternative filter did not meet the required protection time (15 minutes) for higher gas mixture flow rates against the following test gases: phosgene, hydrogen cyanide, and acidic gases such as sulfur dioxide and carbon monoxide. For this reason, additional tests were conducted on filters with an adjusted ratio of activated carbon to hopcalite layers, favoring hopcalite. The results of these sorption characteristic tests on the new filter showed an improvement in protection time against sulfur dioxide, while the protection time against cyclohexane decreased.

These new tests have opened up the possibility for a more detailed researching into the impact of changing the ratio of active filling layers, specifically the homologation of these layers, on the filter's sorption characteristics against all toxic agents. This could serve as a foundational basis for future articles and research in this field.

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