AGING OF THE ASC WHETLERITE TYPE GAS MASK CARBONS DURING STORAGE AND OPERATION – OVERVIEW

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ABSTRACT: *Based on the experience from the storage and operation of the gas masks canisters and filter canisters for collective protection, an overview has been made of one of the main disadvantages of the gas mask carbons used of type ASC Whetlerite, the declining of their protective properties as a result of the "aging' process. The "aging' factors of the gas mask carbons have been considered and mechanisms adopted for deactivation of their active phases. It has been demonstrated that the inclusion of TEDA and derivatives of pyridine in the active phase of the gas mask carbons of the type ASC Whetlerite, only partially solves the problem with the increase of the robustness against "aging" in the conditions of increased atmospheric humidity in operation and storage and for the overall solution, gas mask carbons need to be developed based on impregnation compositions other than of the ASC Whetlerite.*

Keywords: *ASC WHETLERITE TYPE CARBON, "AGING" OF ASC WHETLERITE TYPE CARBON, FACTORS AND MECHANISMS OF "AGING"*

Up to that moment, the widest application in the modern-day gas mask filters, filters employed in collective protection applications (fixed installations, armored vehicles, naval vessels, etc.) due to the good ratio cost-efficiency, has been achieved by the gas mask carbon type ASC Whetlerite. ASC Whetlerite is an activated carbon impregnated with salts of copper, chromium and silver. This material is used by the military to provide protection against chemical warfare agents by either adsorption of the agent or by adsorption followed by chemical reaction with impregnants (primarily toxic agents with relatively low boiling points: hydrogen cyanide, cyanogen chloride, cyanogen) [1].

Regardless of the significant efficiency of the ASC Whetlerite carbons in terms of the toxic agents referred: hydrogen cyanide, cyanogen chloride, cyanogen, one of its main disadvantages is deemed to be the decrease of its protective properties mainly against cyanogen chloride as a result of some extreme conditions such as higher humidity (including pre-adsorbed water), acidic environment, or by usage [2].

The most significant factor for quickly losing of effectiveness i.e. deactivation of gas mask (impregnated) carbon according to Nickolov [3] happens to be the so called "aging" as a result of the impact of the pre-adsorbed water.

This notion has not yet been given any summary and accurate formulation [3]. Unclear problems exist about the mechanism, as well as conditioning factors and consequences of that process. It is known [3] that it mainly affects the active supplements and in parallel, to a less extent, the basic carbon structure.

Assurance in this respect is given by the data [3] demonstrating the alteration of the protective properties against the vapors of cyanogen chloride, as a result of the "aging" (Table 1 and 2).

Table 1. *Impact of the pre-adsorbed humidity by the gas mask carbon type K-5y on the protective properties of the breathing masks EO-14 after 90 days and nights in wet condition*

Quantity of the pre-adsorbed humidity by the gas mask carbon type K-5y in the breathing masks EO-14, g	Sorption capacity of the gas mask carbon of the gas masks EO-14, by the vapors of cyanogen chloride, g	
	immediately after balanced wetting	after 90 days and nights storage in wet condition
about 3, corresponding to 50 % wetting	21	21
about 10, corresponding to 70% wetting	16	7
about 125 -130, corresponding to 90% balance wetting	4	0.3

Table 2. *Alteration of the sorption capacity (g) by the vapors of cyanogen chloride on gas mask carbons as a result of the "aging" process*

Carbon type	"Aging" type	"Aging" conditions	Sorption capacity by ClCN, mg/ml$_{carbon}$
Norit RG 1.5	non-aged (new)	new, received from the Drager company	8.0
Norit RG 1.5	naturally	Drager filter unit CH641 (1970) kept for 13 months under increased humidity (75 %)	4.4
Norit RG 1.5	accelerated	new, artificially "aged" for 10 days and nights under 72°C and relative humidity 90 %	0.6
Portion Type 26	non-aged (new)	Portion filter, new	12.3
Portion Type 26	naturally	Portion filter (1958) kept for 10 years under humidity 75 %	0.8
Pittsburg ASC 12x30	non-aged (new)	kept as required	10.8
Pittsburg ASC 12x30	naturally	Gas mask type A62 (1968) kept for 3 years under humidity 75 %	2.0
Pittsburg ASC 12x30	accelerated	Storage as required, followed by aging for 10 days and nights under relative humidity 90 %	6.4

The tables present gas mask carbons of ASC Whetlerite type, manufactured by different companies however having minor differences by composition of the active phase. The common thing about all carbons considered is the significant decrease of their sorption capacity against the vapors of cyanogen chloride. The combination of the impact of pre-adsorbed water (as a result of the balanced wetting) with increased temperature (sample Norit RG 1.5) minimizes the impact of the storage duration and demonstrates 13 times decrease of the sorption capacity. The continuous storage in wet atmosphere (75 and more %), respectively resulting in the relevant balanced wetting, regardless of the normal ambient temperature, consequently decrease the sorption capacity against the vapors of cyanogen chloride between 2 and 10 times. The storage duration in the conditions of increased humidity can be indicated as an important factor of aging [3].

Significant number of studies have been run on the deactivation of the gas mask carbons, nonetheless, due to its exclusive complexity [4], the mechanism of irreversible decrease of the protective properties by cyanogen chloride as a result of the "aging" has not been clarified up yet. Further complication of the problem stems from the fact that some major supplements (for instance TEDA) can increase the robustness of ASC Whetlerite against the "aging" [5] as, accordingly, their role cannot be explained [2], and also because surface chemistry of the same impregnated carbons is quite complex due to the large number of compounds which can be found on the Cu-Cr impregnated carbon surface [6].

According to all researchers working on the ASC Whetlerite, the active components of the phase represent $Cu(2+)/Cr(6+)$ species. According to Pytlewski [7] several Cu-Cr NH_3 – containing species exist on the surface of Cu-Cr impregnated carbons among which, the most important effect for the removal of hydrogen cyanide, cyanogen chloride, cyanogen has $CuOH.NH_4.CrO_4$. Hammarstrom and Sacco [8] also accept that $CuOH.NH_4.CrO_4$ is the active substance at the impregnated carbon surface for the removal of toxic agents and they revealed that the deactivation under humid atmosphere is due to the conversion of $CuOH.NH_4.CrO_4$ into amorphous brochantite chromate, $Cu_4(OH)_6.CrO_4$, which thereafter decomposes to CuO,

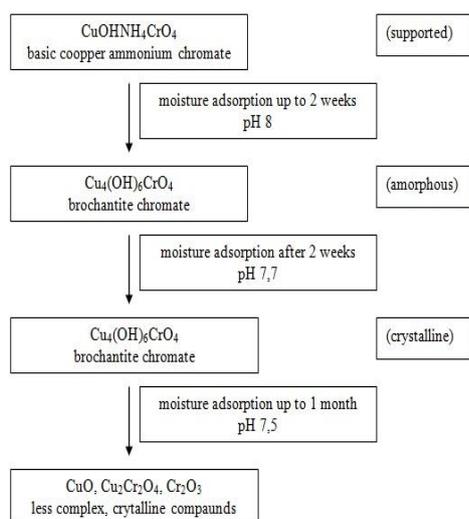$Cu_2Cr_2O_4$ and Cr_2O_3 [6]. This mechanism is shown in Figure 1.

Fig.1. *Moisture deactivation (ageing) mechanism according to Hammarstrom and Sacco,Jr [8]*

The X-ray photoelectron spectroscopy method used by the researchers represents non-alternatively, as a main reason for the deactivation of the ASC Whetlerite type gas mask carbons, the reduction (to various extend) of $Cr^{6+} \rightarrow Cr^{3+}$ and of $Cu^{2+} \rightarrow Cu^{1+}$ surface species.

Brown et al. [9] claimed that the humid environment did not alter the oxidation state of copper, but it leads to reduction of a part of Cr^{6+} (the active species of Cu-Cr impregnated carbon surface) to Cr^{3+}.

In turn, Ehrburger et.al. [6] considered deactivation of Cu-Cr impregnated carbons as two step redox-type reaction. In a first step, chromium species are reduced from oxidation state Cr^{6+} to Cr^{3+} and copper species from Cu^{2+} to Cu^{1+}. Thereafter, monovalent copper compounds are reduced to metallic copper. The latter is observed at elevated temperature. In both cases, the reducing agent is the carbon support itself.

It should be noted, that Cr^{6+} was partially reduced by the carbon support even during the impregnation and/or the drying steps of preparation [6]. Hence the supported chromium species are generally present in the oxidation states +6 and +3 (a minor amount in the general case), as also found by X-ray photoelectron spectroscopy [10].

All studies run in terms of the deactivation of ASC Whetlerite type gas mask carbons prove the importance of the carrier, active carbon in the process referred. According to Deitz et al. [11] carbon is not an inert support. Similarly, Ehrburger et al. [12] assume that the carbon support appears to be the reducing agent of Cu^{2+} into Cu^{1+} and since the rate of aging is strongly increased in presence of water it can be assumed that the reduction of Cu^{2+} (respectively Cr^{6+}) occurs via adsorbed water in micropores of the carbon support.

In the thirties of the twentieth century Dubinin and Zaverina have proven that the active carbons gradually change their properties during storage which, according to [13] is due to the atmospheric humidity and oxygen. The limiting impact of the humidity is emphasized in [3].

All researchers of the problem relate the aging" of the active carbons to the formation of surface oxygen groups (SOG). In accordance with the mechanism adopted by Dubinin [14,15] the sorption capability by water vapors of the active carbons is determined by the hemosorbed oxygen, i.e. by their Surface Oxygen Groups. Hence, the surface oxides are primary adsorption centers for the water molecules. The latter, in parallel with the connection with these centers or amongst them, interact with the carbon surface which results in the increase of its adsorption capability in terms of the atmospheric humidity. Thus, the aging cycle is closed through the increase of the content of surface oxides, respectively to the quantity of sorbed water. According to Tomassi and Neffe [16] the process considered, in a medium of increased humidity content, runs relatively fast.

According to Nickolov [3], the mechanism considered for aging of the active carbons also applies to the gas mask carbons of ASC Whetlerite type, as the active supplements in the latter further assist for the formation of primary sorption centers for water, respectively for the increase of the quantity of water sorbed by the carbons and hence for the aging of the gas mask carbons themselves.

In our opinion, the most exhaustive explanation of the "aging" of the gas mask carbons is given by Saciuk et al.[17]. According to them, the presence of pre-adsorbed water with low alkaline reaction, due to residual ammonia, engenders the dissolving of the active Cu-Cr supplements. Temperature increase (for instance in artificial "aging") accelerates the reduction of $Cr^{6+} \rightarrow Cr^{3+}$, whereat a reductor is probably the basic carbon itself. The evaporation of the pre-adsorbed water is

the onset of the recrystallization of the dissolved compounds. This does not affect the total volume of the micropores of the gas mask carbons, however depending on the type and sizes of resultant crystals can lead to its known redistribution at the account of the supermicropores.

The results from the studies of Hjermsted and Berg [18] confirm Saciuk et al. considering also the fact that dissolving and recrystallizing of active substances of ASC Whetlerite carbons in the capillary-condensed water and the surface –adsorbed water, made the microcrystals grow on the carbon surface, so the contacting area between adsorbate and active substances decreased.

Nickolov, on the basis of unpublished research results claims that in the case of the ASC Whetlerite type carbons obtained in the heat treatment at temperature higher with 20-25° than the technologically accepted, the reduction $Cr^{6+} \rightarrow Cr^{3+}$, under the impact of the pre-adsorbed humidity, runs significantly faster compared to th gas mask carbons obtained while observing the technological conditions.

No effective solutions exist for fighting the aging in conditions of increased atmospheric humidity during operation and storage of ASC Whetlerite type gas mask carbons. Currently to that end, the impregnation ingredients are added up mainly by TEDA [19] (a strong basic compound [2]). To the same end, the Soviet army used pyridine [20], and the American army, besides pyridine, also used picoline [21]. Nowadays, systematic researches of the use of pyridine carboxilic acid as a supplement for the delay of aging of ASC Whetlerite type gas mask carbons are run by J. Lahaye et al. [22]. According to Baker and Poziomek [23], it has been observed that the inclusion of pyridine in the impregnation solutions for obtaining ASC Whetlerite type gas mask carbons results in the reduction of Cr^{6+} to Cr^{3+}, which lowered the interest in the use of pyridine and its derivatives.

As of that moment, regardless of the presence of a series of patents, no effective components exists in the impregnation contents for obtaining ASC Whetlerite type gas mask carbons providing adequately high robustness in terms of aging in the conditions of increased atmospheric humidity during operation and storage.

This, regardless of the good ratio cost-efficiency in ASC Whetlerite type gas mask carbons, necessitates the development of gas mask carbons based on impregnation compositions other than the ASC Whetlarite's, not including Cr^{6+} or its content minimized (>0.6 %) [24].

Conclusion

The widest use in the modern-day gas mask filters and filters employed in collective protection applications are the gas mask carbons of the type ASC Whetlerite. Regardless of the significant efficiency of the ASC Whetlerite carbons in terms of toxic agents such as hydrogen cyanide, cyanogen chloride, cyanogen, one of its main disadvantages is deemed to be the decrease of its protective properties mainly against cyanogen chloride as a result of some extreme conditions such as higher humidity (including pre-adsorpted water), acidic environment, or by usage. The most significant factor for quickly losing of effectiveness i.e. deactivation of gas mask (impregnated) carbon happens to be the so called "aging" as a result of the impact of the pre-adsorpted water. This process mainly affects the active supplements (mainly through the reduction $Cr^{6+} \rightarrow Cr^{3+}$ and much less $Cu^{2+} \rightarrow Cu^{1+}$) and in parallel, to less extend, the basic carbon structure. As of that moment, no effective components exist in the impregnation compositions for obtaining ASC Whetlerite type gas mask carbons providing adequately high robustness in terms of aging in the conditions of increased atmospheric humidity during operation and storage. This necessitates the development of gas mask carbons based on impregnation compositions other

than the ASC Whetlarite's not including Cr^{6+} or its contents minimized.

Acknowledgements

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