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Protective Light Rubberized Material Based on Chlorosulphonated Polyethylene with Increased Resistance to Aggressive Media and Open Flame*

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Abstract

The research was carried out into the development of a light protective flame-resistant rubberized material with a set of protective properties against aggressive media (acids and alkalis), gaseous highly toxic substances (chlorine and ammonia), solvents, and oils. The effect of the composition of rubbers on their protective properties was studied. Rubbers with improved protective properties were prepared on the basis of chlorosulphonated polyethylene combined with chloroprene rubber. A substantial impact of the nature of cross bonds and the type of vulcanizing agent on resistance of rubbers to aggressive media was determined. A series of antipyrenes with a total content of 60 mass parts were developed. They ensure preparation of self-extinguishing rubber upon the preservation of residual durability. A protective lite material with the low surface density and good protecting properties compared to analogues was prepared on the ground of the data obtained.

Keywords: chlorosulphonated polyethylene, vulcanization, protective material, antipyrenes, aggressive media

INTRODUCTION

In recent years, there has been a trend towards increasing the number of emergencies and technogenic catastrophes at chemically hazardous objects. Instances of terrorist attacks committed using highly dangerous technologies, technical means, and materials (chemical, biological, and radiation) and accompanied by human losses and severe economic damage have become more frequent. The increased production and commercial activities also affect the total condition of environmental pollution by hazardous industrial and other wastes.

The need for protection against open flame impact in case of fires at sites and in the residential sector remains relevant.

Only the use of personal protective equipment (PPE) and collective protective equipment may ensure effective security in case of emergency. Personal protective equipment is the most economically accessible and simultaneously effective measure of prevention or reduction of the impact of dangerous chemical and biological factors on the person and human health preservation [1, 2].

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Insulating type protective clothing made of rubberized fabrics ensures the highest degree of protection against vapors and liquid phase (aerosols and drops) of toxic and aggressive substances. The development of new materials with improved functional properties is one of the most crucial areas of developments in this field. These materials also include those intended for the protection of people who work with liquid aggressive and gaseous highly toxic media. Importantly, the materials used during liquidation of consequences of technogenic accidents should be incombustible as well.

One of the monitored indicators of materials to fabricate protective suits is their surface density determining protective suit mass and as a consequence, the duration of continuous work in it.

As demonstrated by analysis of the data available, the used protective rubberized materials of domestic and foreign manufacture have high surface density $(500-600 \text{ g/m}^2)$. This substantially reduces work time in suits made of these materials. Furthermore, during the preparation of protective materials, complex technologies, such as sputtering technique, additional film and adhesion layers, lamination of various type rubbers are used, which complicates their preparation and makes it more costly.

In this regard, the development of a lite (no more than 350 g/m^2) isolating material with increased fire resistance having a set of protective properties against gaseous toxic substances, liquid aggressive media, resistance to oils and solvents, improved performance and ergonomic characteristics, and also the development of permanent or long-term wear PPE based therefrom under conditions of regulatory and repair works at industrial enterprises, upon the threat of man-made accidents or terrorism, pollution, or open flame impact are relevant today.

RUBBERIZED MATERIAL BASED ON CHLOROSULPHONATED POLYETHYLENE

Protecting properties of rubberized materials are primarily determined by the nature of rubber. Considering requirements imposed on protective rubber coatings, rubbers with low gas-penetrability, oil-and-gas resistance, resistance to aggressive media, fire-resistance, and wide temperature operation range are of interest. Furthermore, they should be accessible by cost and produced commercially. Butyl rubber, fluororubber, and especially chlorosulphonated polyethylene (CSPE) fullest meet the listed requirements [3-7]. The latter has high resistance to ultraviolet, ozone, radiation, acids, alkalis, and widely used as in the composition of protective and anticorrosive coatings [8].

As determined in the study of the nature of rubber and cross bonds of vulcanizates based therein on resistance to different aggressive media, CSPE-based rubbers and chloroprene rubber in the 75 : 25 ratio, cured by radiation (γ -radiation Co⁶⁰) and γ -aminopropyltriethoxysilane (AMEO) have the maximum resistance in the most common chemically aggressive media, such as gaseous chlorine and ammonia, concentrated H₂SO₄, HCl, and NaOH [9–12].

In addition to protective properties, rubberized materials should ensure personnel protection from open flame. The increased fireresistance to rubbers under study is given by the use of chlorinated rubbers in its composition. Along with this, CSPE-based rubbers may burn and fully burn down during long open flame impact. In this regard, it is proposed to introduce antipyrenes into the composition of CSPE-based rubbers.

The effect of antipyrenes (both individually and combined) on physicochemical properties

TABLE 1

Dependence of the material fire resistance on the rubber layer mass

Rubber layer mass, g/m ²	Open flame resistance, s	Residual combustion, s
50±5	3±1	2-3
100±5	7±1	2-3
150±7.5	15±1	Absent
250±10	35±1	Absent

Vulcanizing agent type	Surface density, g/m ²	Time of protecti	Time of protective effect, h, no less, under the action of		
		Chlorine	Ammonia		
Radiation	250	10	6		
	350	10	6.5		
AMEO	250	10	7.5		
	350	10	9		

TABLE 2

Material resistance to the action of gaseous highly toxic media

of rubbers and fire-resistance was studied. Fire-resistance includes residual strength of rubbers, *i.e.* the strength that retains in rubbers after open flame impact for 3, 5, and 7 s, and also residual combustion and smoldering. The preservation of residual strength and a lack of residual combustion and smoldering allow preserving performance properties of materials after the cessation of open flame impact.

Antimony trioxide, decabromodiphenyl oxide, ammonium polysulfate, aluminum hydroxide and thermally expanding graphite were used as antipyrenes, selection principle of which is based upon different mechanisms of their action and synergism effects [13–15]. Resulting from the research, there were determined the composition and content (60 mass parts) of antipyrenes ensuring a high level of rubber fire protection: upon open flame impact, rubber withstands up to 7 s, preserving residual strength, while there are no residual combustion and melting, *i.e.* rubber has the property of self-extinguishing.

The optimum compositions of fire-resistant rubbers vulcanized by radiation and AMEO to prepare rubberized materials were determined.

Polyester fiber (surface density of 100 g/m^2) providing the required strength and aggressive resistance of the protective material was selected as fabrics-bases for producing materials. According to its design, the material

is double-sided: on the back side, two layers of rubber coating are applied; on the front – at least five layers (depending on the required mass of 1 m^2 of material).

Materials demonstrated abrasion resistance – no less than 1000 cycles, which corresponds to GOST R ISO 16602–2010 for those used in clothing for chemical protection (not lower than class 3, abrasion resistance of more than 500 cycles).

The effect of rubber coating mass on the properties of the rubberized material was examined. According to the data in Table 1, to prepare a material with the increased fire-resistance, no less than 150 g of rubber per 1 m² of fabrics-bases is required to apply.

Rubberized materials with surface densities of 250 and 350 g/m² were also obtained. Their open flame resistance was determined according to GOST R 12.4.200–99. The fire resistance of the resulting materials was no less than 16 s (AMEO vulcanization) and no less than 20 s (radiation vulcanization).

Material resistance to exposure of gaseous chlorine and ammonia (Tables 2) and liquid aggressive media (Table 3) was studied.

It can be seen that materials vulcanized by AMEO are less stable to the action of a mixture of benzene/ethyl acetate solvents than those vulcanized by irradiation. However, they can be used upon exposure to aggressive media in a lack of solvents.

TABLE 3

Time of protective effect of materials during the impact of aggressive media, solvents, and oil

Type of	Surface density.	Time of protective effect h no less under the action of					
vulcanizing	g/m^2	$\overline{\mathrm{H}_{2}\mathrm{SO}_{4}}$	HCl	NaOH sol.	SZhR-3	Mixture of	Toluene
agent	_			(30%)	oil	petrol/ethylacetate (1:1)	
Радиация	250±10	5	6	6	6	4	5
	350 ± 10	6	6	6	6	5	6
AMEO	250±10	5	6	6	6	2	3
	350 ± 10	5	6	6	6	3	3

As the tests showed, materials vulcanized by radiation demonstrate the most universal protective properties (open flame resistance, the time of protective action, and strength loss during exposure to highly toxic gaseous and liquid aggressive media). There is a good correlation between the results of assessing the resistance of rubberized materials and rubbers to aggressive media.

According to the results of the research, a pilot batch of the rubberized material has been produced using industrial equipment. The material preparation process is based upon layer-by-layer application of a solution of the reaction mixture based on CSPE onto fabric base in a mixture of petrol/ethyl acetate solvents (1 : 1) on the line of application of Siltex rubber coating according to spreading technology. Vulcanization of the resulting material was carried out by radiation using RV 1200 installation (Kazan Synthetic Rubber Plant JSC) with a radiation dose of 150 kGy.

As demonstrated by the comparative analysis of the developed and known industrial materials (T-9t and UNKL-AS), the developed material, with a lower mass, has better indicators according to fire resistance and protective properties against gaseous toxic substances, aggressive media, and solvents (Table 4).

CONCLUSION

Thus, considering earlier elaborated rubbers based on CSPE and chloroprene rubber with high resistance to liquid and gaseous aggressive

TABLE 4

Comparative characteristics of protective materials

Indicators	Materials		
	LPM	T-9t	UNKL-AS
Mass of 1 m ² , g	250±10	620±20	420±20
Breaking load in tension by fabric strips with a width of 50 mm, N $$			
- warpwise	1200 ± 20	1156 ± 20	686 ± 20
– fillingwise	1180 ± 20	793 ± 20	490 ± 20
Tear resistance, N			
- warpwise	22±3	45±3	29±3
– fillingwise	30 ± 3	42±3	24±3
Open flame resistance, s	15 ± 1	N/d	5±1
Abrasion resistance, cycles	1000 ± 30	N/d	N/d
Frost resistance, °C	-40 ± 2	-40 ± 2	-40 ± 2
Time of protective effect against gaseous substances, min:			
- chlorine, concentration (3010 \pm 60) mg/L	200 ± 10	60 ± 10	180 ± 10
– ammonia, concentration (710 \pm 30) mg/L	200±10	60 ± 10	180 ± 10
$^-$ hydrogen sulphide, concentration (1420 $\pm60)$ mg/L	200 ± 10	N/d	N/d
Time of protective effect against liquid substances, min:			
– sodium hydroxide (40 %)	360 ± 20	90 ± 10	60 ± 10
– sulphuric acid (96 %)	180 ± 10	90 ± 10	60 ± 10
– nitric acid (65 %)	240 ± 15	N/d	N/d
– hydrochloric acid (37 %)	360 ± 20	N/d	60 ± 10
– hydrofluoric acid (40 %)	360 ± 20	N/d	Н/д
– SZhR-3 oil	360 ± 20	20 ± 5	10 ± 2
- petrol	360 ± 20	N/d	10 ± 2
- toluene	360 ± 20	N/d	30 ± 5

Notes. 1. LPM – light protective material, T-9t – thermal-resistant material T-9t (NIIEMI JSC), UNKL-AS – the development of KazKhimNII JSC. 2. N/d is no data.

media and fire resistance, a lite insulating material has been developed. It is intended for manufacturing PPE for skin and respiratory organs (including self-rescuers, air bags, and protective clothing) for personnel of chemical industry enterprises and units of the Ministry of Civil Defense of the Russian Federation operating PPE under conditions of probable exposure of open flame and harmful substances, during repair, degassing, and deactivation works, and elimination of consequences of accidents and emergencies.

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