The manufacturing of fire-extinguishing powder materials with specific morphology and hydrophobicity of ammonium phosphates particles

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Introduction

Fire-extinguishing powders (FEP) are the most effective and versatile extinguishing materials which have high specific fire-extinguishing efficiency and capable to extinguish all classes of fire. Nowadays, the main extinguishing component of FEP are ammonium phosphate salts. Their main disadvantages are high hygroscopicity and caking. In addition, powder materials of these salts are obtained by grinding granules that leads to an irregular and angular shape of microsized particles and strong cohesion between them [1, 2].

Within the framework of this research, we used the spray drying method for the synthesis of FEP extinguishing components: ammonium phosphates, magnesium and aluminum hydroxides, which demonstrate significant endothermic effect during their decomposition. Ammonium phosphates emulsion was obtained using heat-resistant (up to 200 °C) surfactants and a hydrophobizing agent based on polysiloxanes, the aqueous emulsions of which make it possible to impart hydrophobic properties to the surface of synthesized particles. The process of spraying drops of emulsion with air temperature at 170 °C and velocity 15 l/min is combined with the subsequent rapid evaporation of water and the formation of powder material particles. Particles of magnesium and aluminum hydroxides were obtained under the same conditions of spray drying from aqueous suspensions. This method makes it possible to obtain polyfunctional extinguishing components particles having a spherical shape and a given size distribution, D(50) = 7 μm.

Hydrophobic silicon dioxide as functional additive for FEP was obtained by the sol-gel process: the hydrolysis of tetraethoxysilane in an ammonia medium followed by modification of a spherical SiO_2 particles surface with a hydrophobic polymethylhydrosiloxane The size of silicon dioxide particles was controlled during preparation based on the Stöber process by variation of the amount of water (mol) in relation to other components. The ratio of components, synthesis time and amount of the hydrophobizing agent were determined to obtain superhydrophobic monodisperse silicon dioxide spherical particles with a size of 50–400 nm and a contact angle of more than 150° [3, 4]. The uniform distribution of the functional additive on the surface of extinguishing components forms a protective coating that prevents caking, reduces the size of agglomerates, and enhances free-flowing properties.

Specific morphology of fire-extinguishing powder particles

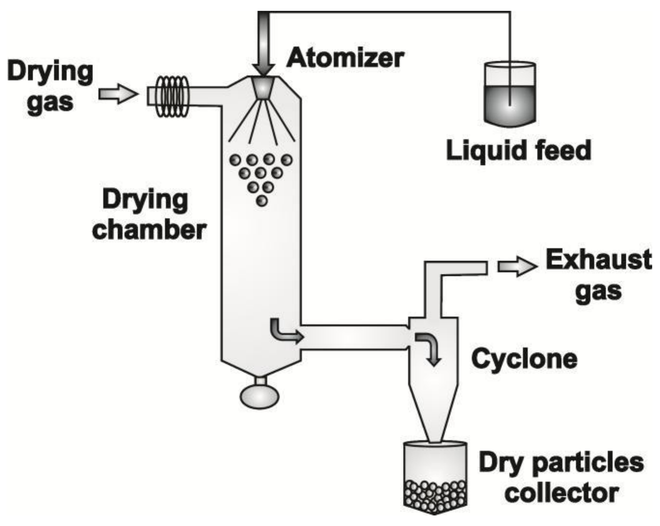
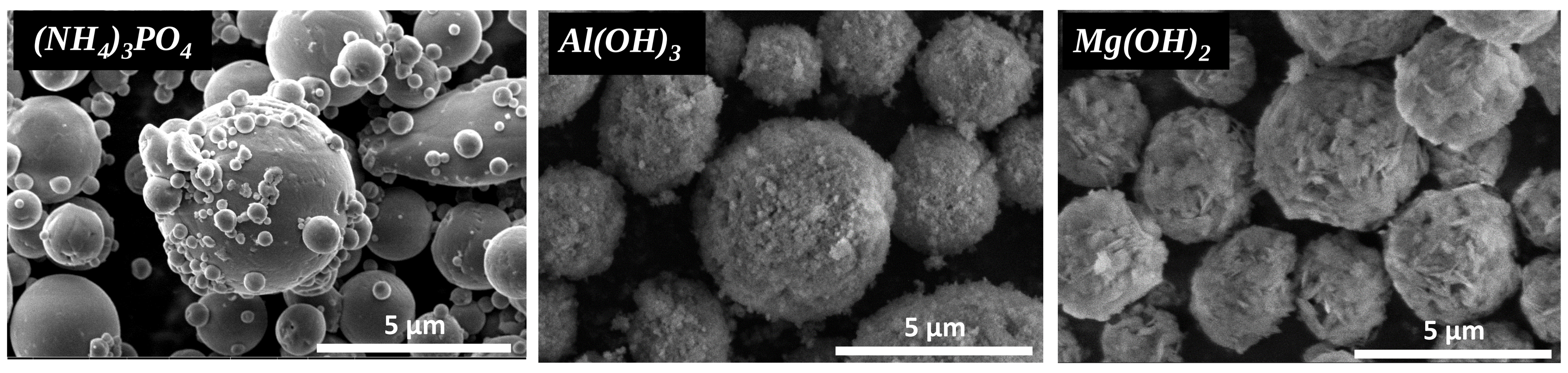
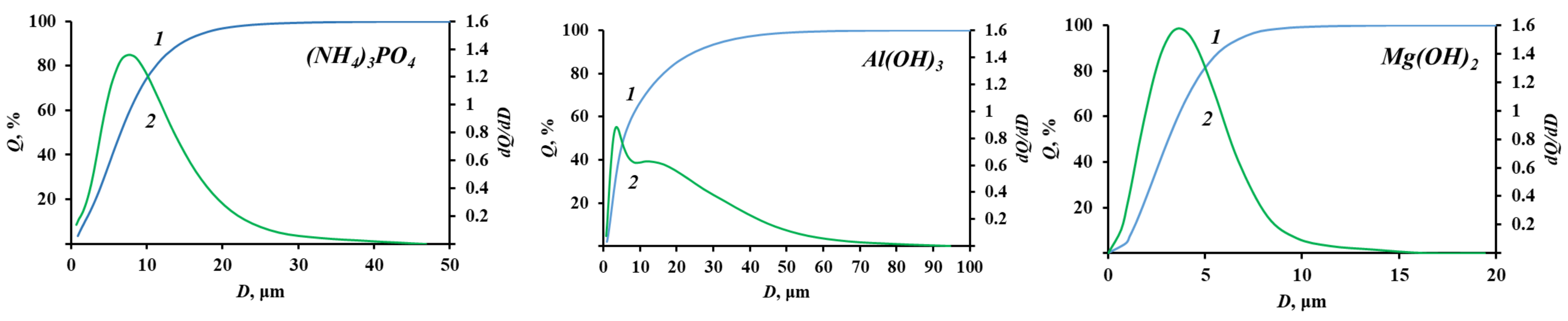


Diagram of the equipment and process of conventional spray-drying [5]

Spray-drying is a rapid, continuous, cost-effective, reproducible and scalable process for the production of dry powders from a fluid material by atomization through an atomizer into a hot drying gas medium, usually air. Often spray-drying is considered only a dehydration process, though it also can be used for the encapsulation of hydrophilic and hydrophobic active compounds within different carriers without substantial thermal degradation, even of heat-sensitive substances due to fast drying (seconds or milliseconds) and relatively short exposure time to heat. The solid particles obtained present relatively narrow size distribution at the submicron-to-micron scale [5].

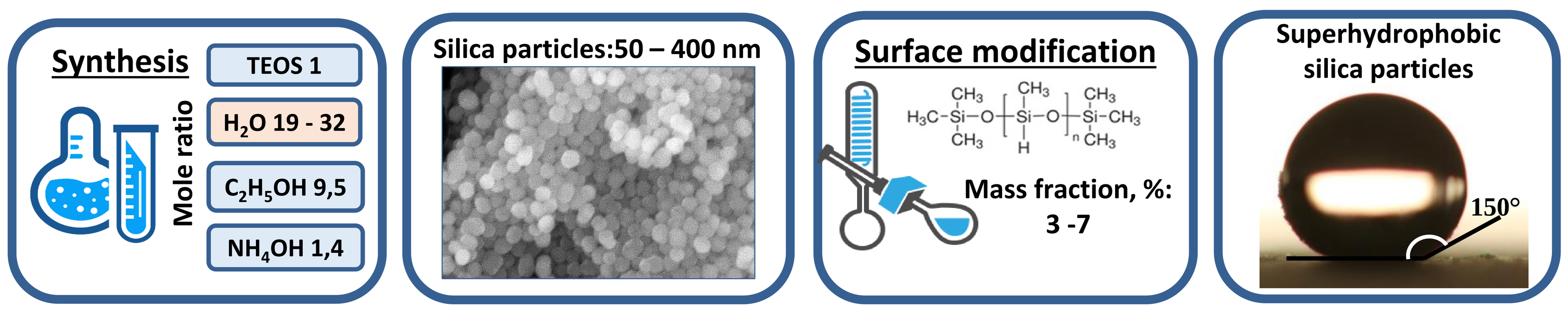


SEM images of fire extinguishing materials particles obtained by the spray drying method

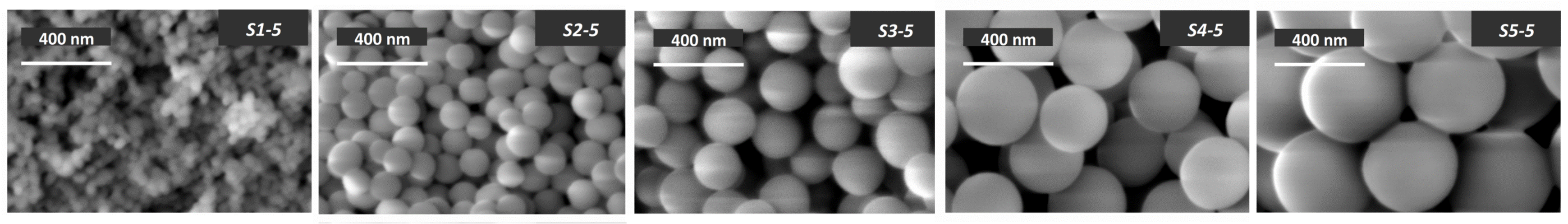


Grain size distribution of synthesized fire-extinguishing materials, where 1—integral distribution, 2—differential distribution

Functional additives for fire-extinguishing powders



The scheme of synthesis and modification of functional additive particles



SEM images of silicon dioxide modified samples

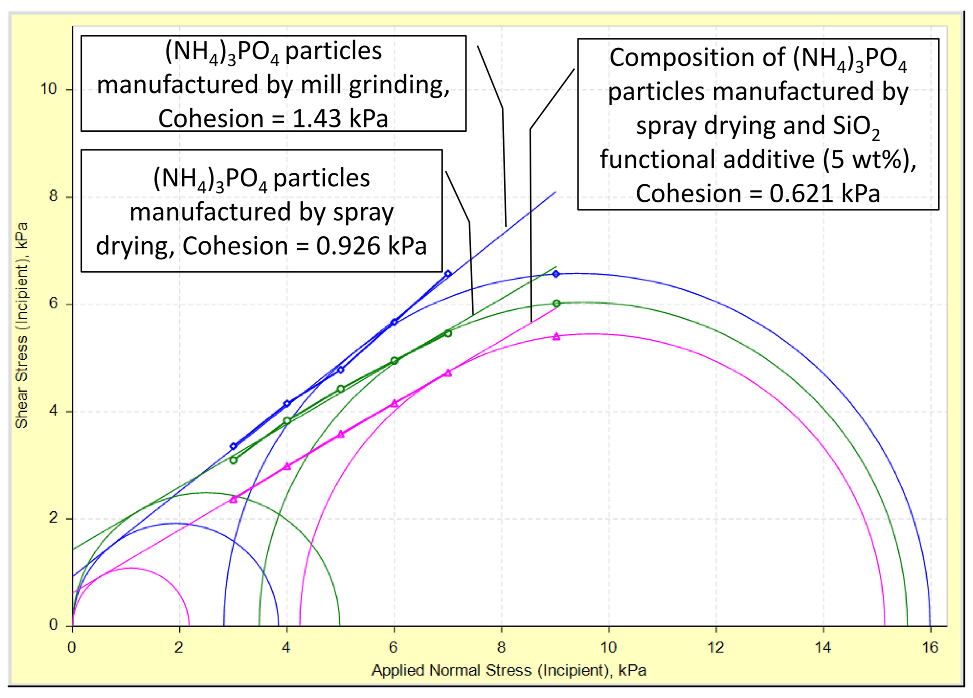
Textural characteristics of initial silicon dioxide samples

Sample	H_2O/TEOS	S_{BET}, m^2/g	$S_{micropores}$ (t-Plot), m^2/g	V_{tot}, cm^3/g	D_{por}, nm	*D*, nm	Mass Loss 200–1000 °C, % (TGA)	Amount of Silanol Groups, mmol/g
S1-0	32	255 ± 5.6	44	0.97	14	50	3.7	4.11
S2-0	28	225 ± 7.6	134	0.37	20	120	3.9	4.33
S3-0	25	232 ± 8.4	151	0.26	18	200	4.1	4.56
S4-0	22	249 ± 9.4	190	0.17	6	300	4.3	4.78
S5-0	19	34 ± 0.26	27	0.05	8	400	4.5	5.00

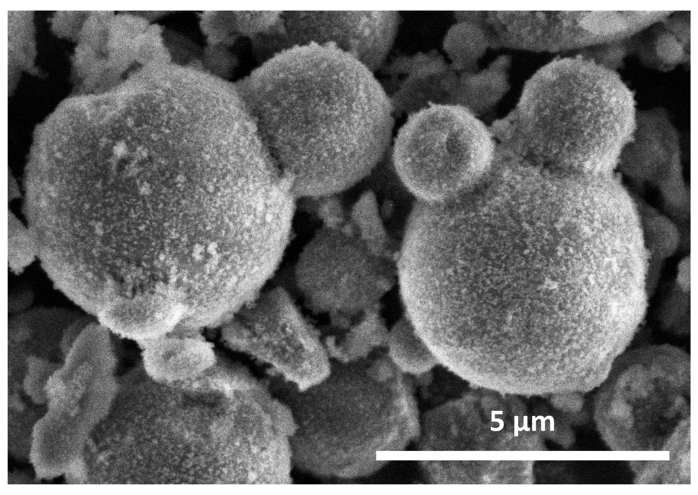
Contact angle for silicon dioxide samples with different particle sizes depending on the amount of PMHS

No	*D*, nm	Amount of PMHS							
		1%		3%		5%		7%	
		No	ϑ, °	No	ϑ, °	No	ϑ, °	No	ϑ, °
S1-0	50	*S1-1*	143.4 ± 1.2	*S1-3*	147.3 ± 1.1	*S1-5*	152.6 ± 1.3	*S1-7*	142.0 ± 1.6
S2-0	120	*S2-2*	143.3 ± 1.6	*S2-3*	144.9 ± 1.8	*S2-5*	146.6 ± 1.5	*S2-7*	142.5 ± 1.6
S3-0	200	*S3-3*	130.4 ± 1.2	*S3-3*	135.8 ± 1.5	*S3-5*	144.6 ± 1.3	*S3-7*	146.4 ± 1.5
S4-0	300	*S4-4*	-	*S4-3*	147.2 ± 1.6	*S4-5*	150.9 ± 1.1	*S4-7*	152.8 ± 0.8
S5-0	400	*S5-5*	-	*S5-3*	158.9 ± 1.7	*S5-5*	160.9 ± 1.6	*S5-7*	157.4 ± 1.5

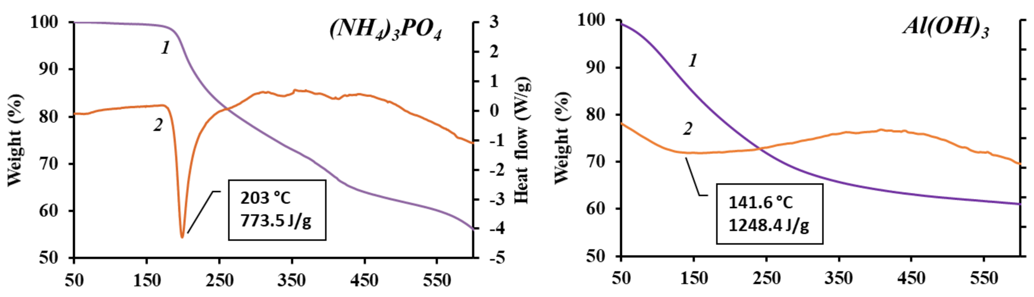
Implementation

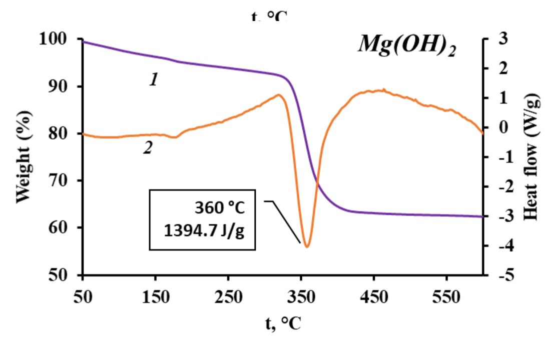


The shear test results of fire-extinguishing powder samples

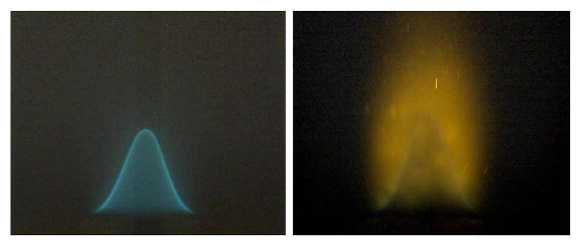


SEM images of fire-extinguishing powder compositions based on $(NH_4)_3PO_4$ and SiO_2 functional additive (d = 50 nm, 5 wt%)

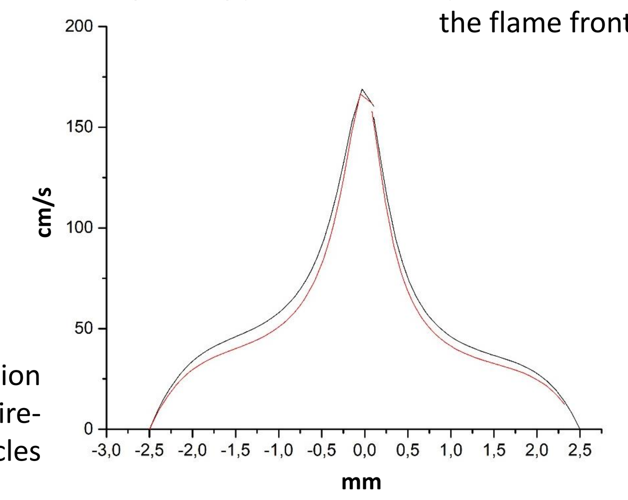




The results of thermal tests of of fire-extinguishing materials samples, where *1* – TGA, *2* – DSC



Extinguishing particles decomposition inside the flame front



Reduction in normal flame propagation speed (red line) after the spraying of fire-extinguishing composition particles

Conclusions

The application of synthesized particles of extinguishing components and functional additives in manufacturing of FEP has improved the following characteristics:

- ✓ Implementation of the spray drying method in elaboration of extinguishing materials provides obtaining of ammonia phosphate, aluminum and magnesium hydroxides particles with spherical shape and certain size distribution that enhance flowability and decrease powder cohesion in comparison with irregular shape particles.
- ✓ Synthesized functional additives based on superhydrophobic silica particles with size 50 – 400 nm allow forming the protective layer on the surface of extinguishing components that reduces powder wettability and decreases capillary forces between particles.
- ✓ Manufactured extinguishing powders demonstrate high endothermic effect of decomposition that enhances the efficiency of combustion processes inhibition by reducing flame propagation speed in short time.

Further work

To develop achieved results, following studies are planned:

- ➢ Development of composite materials consisting of a core based on ammonium phosphate and a shell formed of aluminum or magnesium hydroxides.
- ➢ Elaboration of the surface modification process of aluminum and magnesium hydroxide particles.
- ➢ The study of the flame inhibition process of the developed fire extinguishing compositions.
- ➢ Determination of fire-extinguishing particles shape influence on dynamic characteristics and the coverage area of powders during the spraying process.
- ➢ Characterization of manufactured fire-extinguishing materials rheology to study the effect of particles morphology and their hydrophobicity degree on cohesion and its change during the aeration process.

Literature

[1] Kondrashova, N.B.; Valtsifer, I.V. Control over rheological properties of powdered formulations based on phosphate-ammonium salts and hydrophobized silicon oxide. *Russ. J. Appl. Chem.* **2017**, *90*, 1592–1597. DOI: 10.1134/S1070427217100068

[2] Kondrashova, N.B.; Shamsutdinov, A.S. Hydrophobized silicas as functional fillers of fire-extinguishing powders. *Inorg. Mater.* **2018**, *54*, 1078–1083. DOI: 10.1134/S0020168518100102

[3] Saenko, E.V.; Huo, Y. Mesoporous hydrophobic silica nanoparticles as flow-enhancing additives for fire and explosion suppression formulations. *ACS Appl. Nano Mater.* **2020**, *3*, 2221–2233. DOI: 10.1021/acsanm.9b02309

[4] Shamsutdinov, A.Sh.; Kondrashova, N.B. Manufacturing, properties, and application of nanosized superhydrophobic spherical silicon dioxide particles as a functional additive to fire extinguishing powders. *ACS Ind. Eng. Chem. Res.* **2021**, *60*, 11905–11914. DOI: 10.1021/acs.iecr.1c01999

[5] Alejandro Sosnik, Katia P. Seremeta, Advantages and challenges of the spray-drying technology for the production of pure drug particles and drug-loaded polymeric carriers. *Adv. Colloid Interface Sci.* **2015**, 223, 40-54. DOI:10.1016/j.cis.2015.05.003.

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