AA34 – New Products from RUSAL's Super-Fine Precipitated Aluminum Hydroxide

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Abstract

UC RUSAL is currently developing production of aluminum hydroxide products for non-metallurgical applications. One of the prospective products is super-fine precipitated aluminum trihydroxide VOGA, which is used as a halogen-free fire retardant, smoke suppressant and filler for cable insulation and other polymeric materials. RUSAL produces VOGA using its own proprietary process. The product is characterized by narrow particle size distribution; the average grain size is 2 µm and can be adjusted depending on the customers' requirements. The production process is truly promising and allows obtaining aluminum hydroxide that can be used as a raw material for catalyst carriers in oil industry, as well as for some other applications, i.e. synthetic floor coatings, artificial stone, mechanical rubber goods, fire-retarding compositions.

Keywords: Super-fine precipitated aluminum trihydroxide, Special aluminum hydroxide, Fire retardant, Functional filler.

1. General Remarks

Super-fine precipitated aluminum trihydroxide (SF ATH – VOGA) is one of the most promising and effective halogen-free mineral fire retardant and filler to reduce the fire hazard rating of polymeric materials [1–7]. Primarily, it can be applied for non-combustible halogen-free cable insulation based on polyethene, ethylene-vinyl acetate or polyvinylchloride. In the polymer matrix, having the loading efficiency of 30–70 %, said fire retardant acts by thermal decomposition reaction to separate water (in form of steam):

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \quad (1)$$

Aluminium hydroxide is characterized by the following fire-retardant properties:

- early thermal dehydration (at 190–225 °C);
- significant heat absorption (1051 J/g);
- high oxygen index;
- effective smoke suppression;
- reduction of the toxic properties of the flue gases.

Electrical cables insulated using fire-retardant aluminium hydroxide must or should be used under the most stringent requirements for the fire safety, i.e. critical industries, aircraft- and shipbuilding, in premises and facilities with mass presence of people (schools, hospitals, malls, etc.)

For this purpose, in 2022 RUSAL launched the production of super-fine precipitated aluminum trihydroxide with average particle size (D50) of 1.5–3.5 µm for cable compounds using the proprietary sol-gel process.

Furthermore, the process proved to be flexible in terms of controlling the phase composition and particle size distribution by changing the temperature and fluid dynamics of solution mixing process. Bayerite content in the product can vary within 50–95 %, and the average particle size (D50) can range within 1.2–20 µm. It allowed expanding the use of aluminium hydroxide produced by the sol-gel process; namely, it can be applied in the products used for the following:

- fillers in the composites based on the epoxy, polyester, polyisocyanate and other polymer resins to be used in transportation, insulators, etc. (GAM – fine aluminium hydroxide);
- floorings;
- fire retardants for construction;
- paints and varnishes;
- bayerite precursors for catalyst carriers and adsorbing agents (GAK – catalytic aluminium hydroxide).

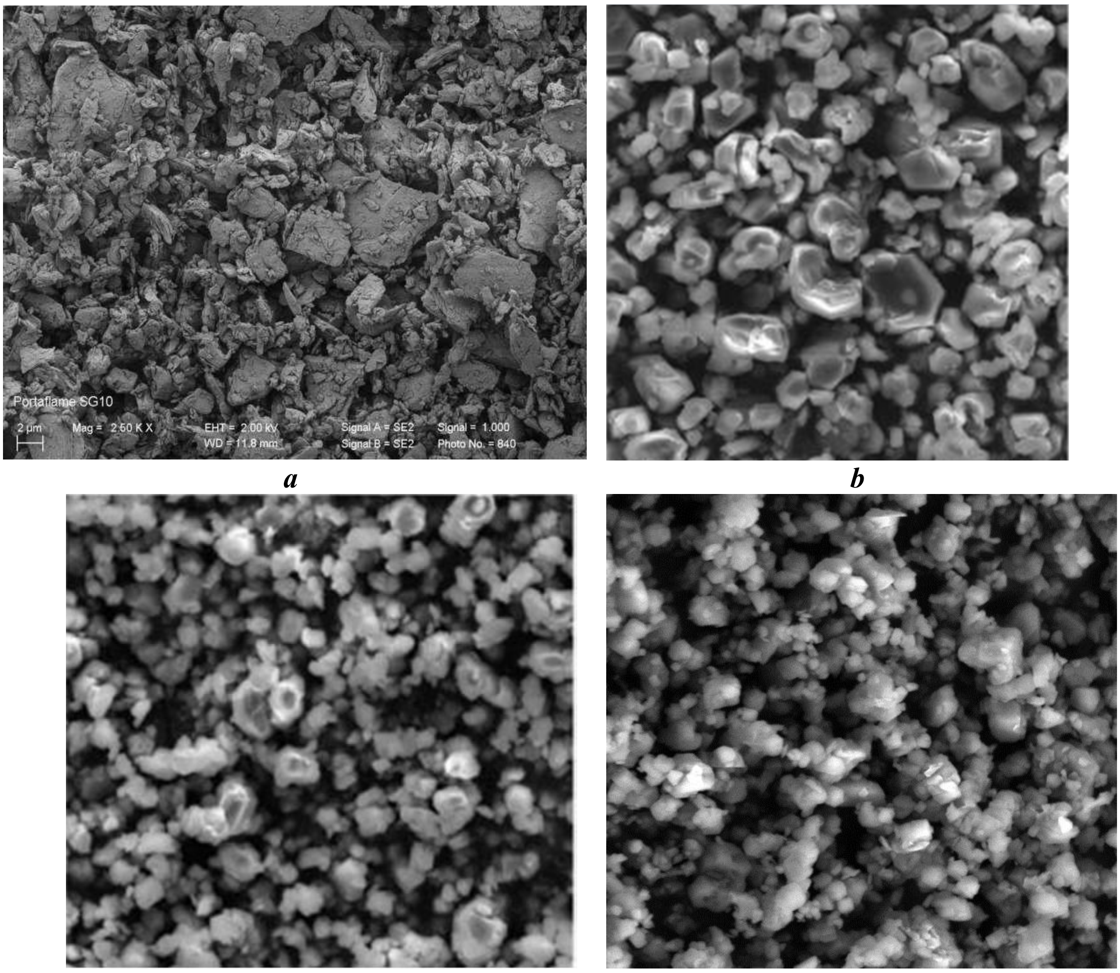
However, use of aluminium hydroxide instead of magnesium hydroxide, which decomposes at a temperature of 320 °C, can be quite challenging for producing compounds, as a higher temperature of polymer blend processing enables to improve the efficiency of extrusion equipment. Thus, one should find a good balance between the early thermal dehydration and processing properties of aluminium hydroxide.

Leading European and American manufacturers of aluminium hydroxide adopt various approaches to this issue. Some of them improve thermal stability by controlling the crystalline structure and increasing the size of the particles, and others enhance rheology by mixing aluminium hydroxides of different particle size distribution. Nevertheless, all manufacturers provide their customers with specific compound blends to ensure proper processing and preserving the best fire-resistant properties of the cables.

It should be noted that the admissible temperature of obtaining and further processing of the compounds results from both properties of the source polymers and the viscosity of the material. In actual production, this temperature is maintained by controlled heating of the polymer, but additional self-heating occurs due to mechanical friction during the stirring of the compound with the fire-retardant filler in the screw extruder. In this case, the rheology of the powder is important attributed to its particle size distribution, shape of the particles, and the presence of special coupling agents, compatibilizers and coating components on the surface, included into the compound blend. The mechanical self-heating increases the temperature of the mix and the thermal dehydration of the fire retardant begins thus resulting in formation of the pores due to boiling the free water.

Particle size distribution and particle shape of the filler characterize the viscosity of the compound and the intensity of the internal friction during the passing of the screw extruder, thus producing significant influence on the self-heating of the compound. It is known that the higher particle size distribution of the filler (mineral fire retardant) increases the viscosity of the blend. Besides, the viscosity of the compound increases due to the use of aluminium hydroxide obtained by grinding a larger product (smelter grade hydrate). Such grinded aluminium hydroxide is characterized by the particles of irregular shattered shape [8] (see Figure 1 (a)) that increases the internal friction.

For this reason, aluminium hydroxides precipitated from the pregnant liquor and characterized by hexagonal, prismatic or tabular particles are mainly used as fire retardants for cable insulation (Figure 1 (b), (c), (d)).



a ***b***

c ***d***

Figure 1. SEM photograph of third-party commercial fire-retardant aluminium hydroxides (for b, c and d samples field of vision is 20 µm).

The preliminary analysis of SEM photographs shows that samples b, c and d have the hexagonal shape similar to gibbsite. Particle size in the field of vision of sample b ranges from 0.5 to 5 µm mostly of 2.0–2.5 µm. Samples c and d are characterized by smaller particles, i.e. mostly of 1–1.5 µm. However, the amount of agglomerates in the field of vision is high.

Table 1 presents the particle size distribution and BET surface area of samples b, c and d. Particle size analysis proves that samples b, c and d show the correlation between the particle size distribution and the surface area. Some Russian manufacturers of the compounds state that sample b demonstrates the best processing properties and application of sample c have the highest oxygen index (OI). Therefore, high particle size distribution and specific surface provide for even distribution of the fire retardant in the compound, but on the other hand, they increase the connection between the filler and polymer matrix thus resulting in increasing viscosity and decreasing processing properties of the compound.

Table 1. Some quality parameters of commercial fire-retardant precipitated aluminium hydroxide by third-party manufacturers.

Sample	Particle size distribution, µm				Specific surface, m^2/g
	D10	D50	D90	D99	
b	0.68	1.54	3.21	5.56	5.2
c	0.82	1.91	3.59	4.49	3.2
d	0.78	1.63	3.38	7.2	4.5

The present paper presents one of the methods to control the shape of fine particles of fire retardant aluminium hydroxide produced by RUSAL's sol-gel process to reduce the specific surface and improve the rheological properties.

Initially this process [9] included mixing an alkaline pregnant liquor and neutralizing solution; said neutralizing solution being an aqueous solution with the density of 1100–1300 kg/m^3 and containing bicarbonates and carbonates of alkali metals. The liquor was neutralized to achieve $Na_2O_{caustic}$ content of 1–15 g/L. It allowed obtaining fine aluminum hydroxide particles (predominantly, bayerite) of a specific size range, i.e. 0.7–3 µm. Therefore, fine particles generated within 15–30 minutes as compared with hours as per the standard process; besides, submicron seed is not used. However, the first batches of the product were characterized by the wide range of particle sizes and irregular, mostly elongated shape and presence of agglomerates that resulted in high viscosity of the polymer blends and deteriorated the stress-strain properties of the compounds.

The process was gradually upgraded [10]. It was decided to stir the mixture of the solutions in the reactor for at least 30–240 minutes when subjected to the shear rates of the liquid phase of 10–210 s^{-1}. Therefore, aluminium hydroxide was obtained having rounded particles. Besides, the average particle size (D50) is no more than 10 µm and the size range is quite narrow.

Control of 1.2–20 µm particle shape is a challenging task. Nevertheless, RUSAL's sol-gel process enables to solve this issue using a simple process solution, i.e. maintaining specific hydrodynamic conditions during the sol-gel transition.

2. Experimental

An experiment on obtaining aluminium hydroxide with rounded particles was carried out in 200 L batch reactor equipped with a blade type agitator and fixed impingement plates. The experiment used the pregnant liquor from RUSAL's Achinsk refinery, which operates by sintering process, and a sodium bicarbonate solution. Said pregnant liquor had the following composition: 75 g/L Al_2O_3; 70.6 g/L $Na_2O_{caustic}$; 73.1 g/L Na_2O_{total}. The sodium bicarbonate solution was obtained by gassing a sodium solution with flue gases from the sintering kilns and contained 89 g/L Na_2O_{total} and 91.8 g/L $NaHCO_3$.

Hot pregnant and sodium bicarbonate solutions were added to the reactor in proportion to obtain the residual content of 10 g/L $Na_2O_{caustic}$. The resulting slurry was held while stirring for 45 minutes at the shear rate of > 10 s^{-1}. Then, aluminium hydroxide was thickened, filtered, washed, and dried.

Particle size distribution was determined with the laser diffraction method using Microtrac S3500. Sieve residue was analyzed by sieve analysis.

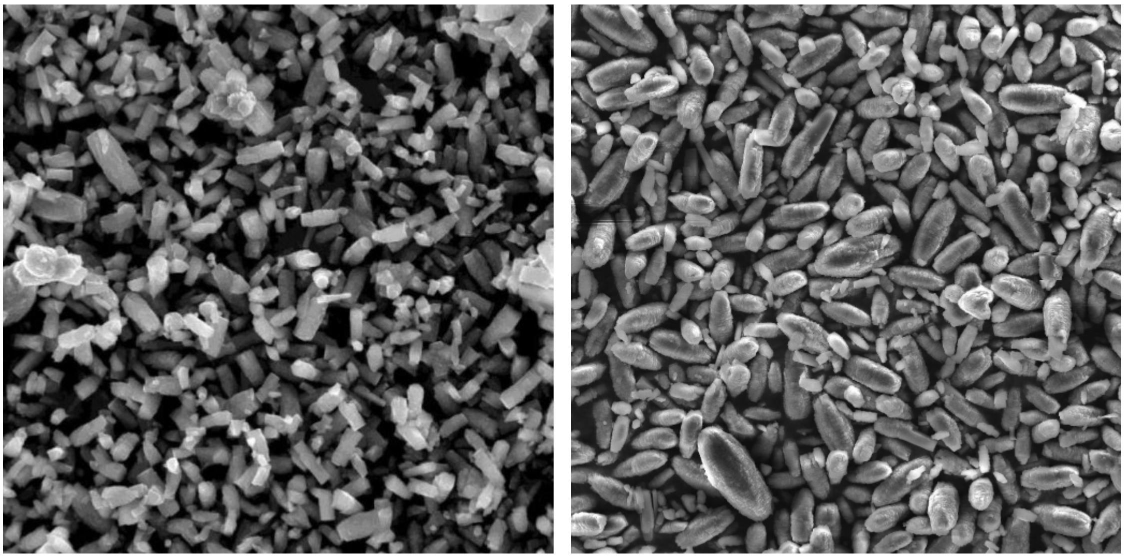
Particle morphology was examined using TESCAN scanning election microscopes (MIRA 3 and VEGA Compact).

Other parameters were analyzed by the specialists of compound manufacturers.

Batches of super-fine precipitated aluminum trihydroxide VOGA 205 obtained before and after introducing the new particle shape control method were used for reference.

3. Discussion

Figure 2 shows the morphology of the particles and Table 2 presents the quality properties of VOGA 205 fire retardant from the pilot, test and commercial batches.



Sample 1 (pilot) **Sample 2 (test)**

Sample 3 (commercial)

Figure 2. Morphology of VOGA particles in course of improving the product particles (field of vision of 20 µm).

Table 2. Quality properties of the samples of fire retardant with different shape of the particles.

Sample	Particle size distribution, µm				Specific surface (BET), m^2/g	Weight percent of 45 µm sieve residue, %	Bulk density, kg/m^3
	D10	D50	D90	D99			
1	0.65	1.91	14.88	101.3	4.5	6.3	308
2	1.21	2.66	4.95	9.11	2.5	≤0.1	452
3	1.01	2.05	3.54	4.56	2.3	≤0.1	368

It is evident that VOGA 205 product significantly improved.

The particles of the test sample showed the best shape but 45 minutes holding of the slurry while stirring results in particle coarsening and requires additional equipment. Currently, rounding of the particles occurs during the sol-gel transition in the kneader of the special design but with the standard operating principle. Less rounded shape of the particles did not affect the rheology, fire-retardant or processing properties of the powder.

All samples were tested by the prospective customers to synthesize the compounds based on the ethylene-vinyl acetate with 50 % aluminium hydroxide filler. The following parameters were evaluated: melt flow index of the polymer with the filler and stress-strain properties of the compound, i.e. breaking elongation and tenacity. Table 3 shows that rounded samples demonstrate better performance as compared with the pilot material. Besides, unrounded sample does not comply with the values required by the compound manufacturers in terms of breaking elongation and melt flow index.

Tests conducted by the compound manufacturers proved that less rounded shape of the particles in the commercial batch did not affect the rheology and processing properties of the product (Table 3).

Table 3. Processing properties of the fire retardants.

Property	Customers' requirements	Sample 1	Sample 2	Sample 3
Tenacity, MPa	≤ 10.5	10.8	11.0	11.1
Breaking elongation, %	≤ 150	135.2	176	172
Melt flow index (160/21.6)	≤ 5	3.3	5.3	5.2
Density, g/cm^3	1.51	1.52	1.51	1.51

In addition to achieving all required stress-strain properties, the melt flow index, which characterizes the viscosity of the polymer compound, also significantly improved. Moreover, self-heating in the extruder decreased. It allowed avoiding pore generation in the compound due to thermal decomposition of aluminium hydroxide while maintaining thermal stability of commercial fire retardant at 205–207 °C.

Better shape of VOGA particles within the range of D50 3.5–20 µm also improved the processing properties of the products designed to fill other polymer materials. For example, GAK product containing > 85 % bayerite and with average particle size of < 2 µm shows better extrusion performance after peptization as compared with available analogues.

4. Conclusions

Sol-gel process, which is implemented at RUSAL's Achinsk refinery, enables to obtain powders of super-fine precipitated aluminum trihydroxide using one process stage; said powders having good fire-retardant properties that can be used in cable insulation of low fire hazard based on halogen-free and PVC compounds.

The new process allows controlling phase composition and particle size distribution by varying the temperature and hydrodynamics of the mixing of the solutions. Bayrite content in the product can range within 50–95 % and the average particle size (D50) can vary within 1.2–20 µm that provide for new applications of the product: floorings, solid surfacing, rubber goods, paints and varnishes, fire-retardant construction materials, composites, etc.

Temperature limitations for producing halogen-free cable compounds with low fire hazard can be avoided by improving thermal stability of the mineral fire retardant and enhancing the rheology of the powder due to the roundness of its particles. Additionally, it reduces the viscosity of the polymer compounds, which can be used for other applications.

RUSAL's process enables to obtain round fine particles of fire retardant using easy and effective method by the specific hydrodynamic conditions of mixing the solutions.

Acknowledgement

The authors are grateful for the assistance in development of the process and preparation of this paper to Dmitry Kibartas, Vladimir Bayanov and the specialists of the production facility of fire retardant and research laboratory of RUSAL's Achinsk Alumina Refinery.

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