

Influence of Layered Silicates 1:1 on PTFE Properties

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Abstract – The results of the study of physical and mechanical and tribological properties of PTFE-based composites with addition of serpentine and kaolin are described. Magnesium spinel was used as a functional additive. Improvement of the characteristics of the material due to mechanical activation of the fillers increasing adhesive interaction between components of the composite material was identified. Methods of capillary electrophoresis and atomic adsorption spectroscopy revealed an increase in the number of active cations due to mechanical activation. The IR-spectroscopy identified that the cause of an increase in the number of cations is destruction of octahedral networks of fillers subject to mechanical activation. It is assumed that high coordination activity of aluminum ions which are part of magnesium and kaolin spinels relative to the fluorine atoms of PTFE macromolecules and oxygen atoms on the surface of mechanically activated layered silicates, intensifies interfacial interaction.

Keywords – PTFE; layered silicates; kaolin; serpentine; magnesium spinel; tribological properties; mechanical activation.

I. INTRODUCTION

Among polymeric materials used in difficult operating conditions, the most promising one is polytetrafluoroethylene (PTFE) which has unique chemical inertness, high thermal and frost resistance, high strength characteristics and low friction. However, PTFE has a number of disadvantages (low wear resistance, high linear thermal expansion, deformation under low loads).

The method used for improving physicochemical and antifriction properties of PTFE is its modification with various

fillers which helps produce materials with new technological and operational properties.

One of the promising areas of production of polymer nanocomposites is the use of mineral layered silicates (CC) or clay minerals as fillers. Nanoparticles are uniform in size and have a flocculent shape, which improves mechanical properties of nanocomposites. Due to the layered structure, they can act as solid lubricants on the friction surface of composites. In addition, the source material is available.

As a result of mixing PTFE and polymers, the size of the particles can reach 1 nm and their diameter will vary from 250 to 1000 nm. Due to the nanometer particle size achieved by dispersion, nanocomposites based on layered silicates exhibit significantly improved mechanical, thermal, optical, and physicochemical properties compared to a pure polymer or a traditional filled polymer with a low filler content. Properties can be improved by increasing the modulus of elasticity, strength, heat resistance, or decreasing gas permeability and flammability [1–4].

II. MATERIALS

PN-90 polytetrafluoroethylene (PTFE) produced by Galopolymer Perm was used as a basis for the composite. The average particle size was 21–45 microns.

PTFE $(-C_2F_4-)_n$ has rare physical and chemical properties and is widely used as a tribotechnical material for producing parts of friction units and as sealing agents and sliding bearings in equipment of the chemical and petrochemical industry.

The following fillers were used:

- serpentine (S) of the Khamelovsky field, Murmansk region. Serpentine belongs to the group of magnesium water silicates and has the chemical formula: $Mg_6(OH)_8[Si_4O_{10}]$;
- Kaolin (K) of the Altai field is a clayey mineral from the group of water silicates. The mineral composition of kaolin: kaolinite (~ 40%), montmorillonite (~ 16%), quartz (25%), orthoclase (~ 15%) and albite (~ 6%). The kaoline formula is $Al_2[Si_2O_5](OH)_4$.
- magnesium nanospinel (MS) is a binary oxide with the chemical formula: $MgAl_2O_4$. Average sizes are 70-80 microns.

The structure of layered silicates is a grid of silicon-oxygen tetrahedra alternating with a grid of octahedra of Al (OH) 3 gibbsite or brucite Mg (OH) 2, which form a layer packet. There are two main types of packages.

- two-layer 1: 1 asymmetrical;
- three-layer 2: 1 symmetrical

The asymmetrical 1: 1 package consists of a single tetrahedron grid with the formula $[(Si_2O_5)(OH)]$ and a grid of octahedra filled with magnesium (serpentine) or aluminum (kaolinite) atoms. Packages are shifted relative to each other. In each packet, magnesium and aluminum occupy octahedral positions, being located between the O_2 atoms and hydroxyl (OH) groups [5].

III. METHODS

PTFE was dried, grinded and sieved. The fillers were mechanically activated in the "Activator - 2 S" planetary mill at a speed of 1356 rpm and acceleration of 150 g; the processing time was 2 minutes. Then, activated MS was added to the mechanically activated SS. The mixture of fillers was gradually introduced into a part of the polymer matrix at a ratio of 50:50 and then added to the rest of the PTFE. The components were mixed at a high speed. Testing samples were produced from the mixture. Samples were obtained according to the technology of cold molding at a pressure of 50 MPa (pressing speed was 0.45 MPa/s, standing time under pressure was 2 minutes). The samples were sintered in molds at a temperature of 350–380 °C.

Deformation-strength characteristics of composites are as follows: ultimate strength, relative elongation (GOST 11262-80), modulus of elasticity (GOST 9550-81). They were determined using Autograph AGS-J (Shimadzu, Japan) at a room temperature.

The wear rate and friction coefficient were determined using CETR UMT-3 (USA) according to the friction scheme "finger-disc" at a load of 160 N, a sliding speed of 96 rpm during 1.5 hours and 4 hours. The wear rate was assessed by weight loss of the samples per unit time.

The IR spectra of the samples were measured using Varian 7000 FT-IR Fourier (USA). Spectra were determined using the ATR in the range of 550-4000 cm^{-1} . For comparison, analysis of the samples was carried out before and after friction.

The method of capillary electrophoresis (CE) was used to determine the number of mobile cations of magnesium in aqueous extracts of SS before and after mechanical activation. Analysis of the quantitative and qualitative composition of water extracts from the SS was carried out using Capel 105 (Russia) and "Multichrome 1.52y". Mobile aluminum cations were determined by an atomic adsorption method with electrothermal atomization using Lumex (Russia).

IV. RESULTS

The results of the study of physical and mechanical properties of PTFE-based composites depending on the share of kaolin, serpentine and MS are presented in Tables I and II.

TABLE I. PHYSICAL AND MECHANICAL PROPERTIES OF PTFE-BASED COMPOSITES DEPENDING ON THE CONTENT OF KAOLIN AND MS

Composite	$\Delta\epsilon_p, \%$	$\Delta\sigma_p, MPa$	E, MPa
PTFE	320	20,0	479
PTFE +2%K	507	20,9	440
PTFE +1,5%K+0,5%MS	373	20,9	516
PTFE +1,8%K+0,2% MS	378	20,7	505
PTFE +5%K	457	16,0	504
PTFE +4,0%K+1,0% MS	332	15,8	453
PTFE +4,5%K+0,5% MS	395	15,6	536
PTFE 4,8%K+0,2%MS	440	14,1	880

TABLE II. PHYSICAL AND MECHANICAL PROPERTIES OF PTFE-BASED COMPOSITES DEPENDING ON THE CONTENT OF SERPENTINE AND MS

Композит	$\Delta\epsilon_p, \%$	$\Delta\sigma_p, MPa$	E, MPa
PTFE	320	20,0	479
PTFE +2%S	316	14,0	518
PTFE +1,5%S+0,5% MS	379	17,1	502
PTFE +1,8%S+0,2% MS	321	16,1	504
PTFE +5%S	272	13,0	575
PTFE +4,0%S+1,0% MS	265	12,5	605
PTFE +4,5%S+0,5% MS	137	9,1	595
PTFE +4,8%S+0,2% MS	135	9,6	397

a.Note: $\Delta\epsilon_p$ – breaking elongation; $\Delta\sigma_p$ – breaking tensile stress; E – modulus of elasticity.

Comparison of the physical and mechanical characteristics of PCM revealed that additional introduction of MS (within 2 wt.%) intensifies strain-strength characteristics of PCM. Increased concentration of the filler weakens these characteristics. This change is characteristic of PTFE and depends on the nature of the effect of the filler on flexibility and conformational changes of the macromolecule of the polymer matrix depending on dispersion, concentration and chemical nature of the filler [6]. Kaolin composites are characterized by an increase in the elastic modulus, which is accompanied by an increase in elasticity while maintaining or increasing the

breaking tensile strength. Even with a further increase in the filler content, the modulus of elasticity and elasticity remain high. The similar phenomenon is usually observed in polymer dispersed nanocomposites due to a sharp increase in the contact area between nanofiller particles and polymer macromolecules. It is a nanoadhesion effect [7].

The properties are weakened due to an increase in rigidity of molecules interacting with the modifier within the amorphous phase, an increase in brittleness and a decrease in strength [8]. This is typical of conventional composites, when the areas of contact with the segments of the macromolecule between the polymer macromolecule and the micro-dimensional filler are limited by the projections or roughness of the filler. The relaxing ability of matrix macromolecules decreases due to internal stresses [9, 10], i.e., these results are due to agglomeration of the filler.

Tables I and II show that the modulus of elasticity in almost all composites is higher than that of the original PTFE. It is known [11] that introduction of dispersed fillers increases the modulus of elasticity, and the absence of interfacial adhesion in the structure of the polymer matrix – the filler – decreases it. Thus, deformation-strength characteristics of the composites show that these composites are characterized by high interfacial interaction.

Addition of kaolin and MS improved wear resistance by 1250 times, addition of serpentine and magnesium spinel increased it by 1125 times (Tables III, IV). It is well known that in the process of friction, the surface layers experience significant pressure and shear stresses. The mechanochemical destruction of macromolecules causes rupture of bonds, generation of free radicals, and adsorption plasticization of both the polymer and its conjugate metal counterbody [12, 13]. Along with high temperatures, these processes cause formation of an intermediate phase separating the rubbing surfaces. In [14], the authors show that friction causes formation of a plastic layer of a new phase consisting of particles of oxidized polymer fragments and silicate which prevents abrasion of the base material and improves wear resistance.

TABLE III. TRIBOTECHNICAL CHARACTERISTICS OF PTFE-BASED COMPOSITES DEPENDING ON THE CONTENT OF KAOLIN AND MS

Composite	$I_{run}, mg/h$	$I, mg/h$	f
PTFE	112,48	65,61	0,23
PTFE+2%K	1,92	0,23	0,33
PTFE+1,5%K+0,5%MS	0,98	0,13	0,24
PTFE+1,8%K+0,2%MS	1,14	0,18	0,22
PTFE+5%K	0,77	0,12	0,32
PTFE+4,0%K+1,0%MS	1,56	0,15	0,27
PTFE+4,5%K+0,5%MS	0,21	0,13	0,27
PTFE+4,8%K+0,2%MS	0,49	0,09	0,23

TABLE IV. TRIBOTECHNICAL CHARACTERISTICS OF PTFE-BASED COMPOSITES DEPENDING ON THE CONTENT OF SERPENTINE AND MS

Composite	$I_{run}, mg/h$	$I, mg/h$	f
PTFE	112,48	65,61	0,23
PTFE+2%S	1,75	0,10	0,32
PTFE+1,5%S+0,5%MS	0,77	0,16	0,25
PTFE+1,8%S+0,2%MS	0,85	0,10	0,24
PTFE+5%S	0,59	0,14	0,32
PTFE+4,0%S+1,0%MS	0,35	0,14	0,26
PTFE+4,5%S+0,5%MS	0,91	0,13	0,26
PTFE+4,8%S+0,2%MS	0,95	0,10	0,27

b.Note: I_{run} – mass wear rate during running-in; I – the rate of mass wear after running-in; f – coefficient of friction after running-in.

It can be seen that wear resistance of materials depends on the ratio of layered silicates to MS. Analysis of the results shows that an increase in the share of MS weakens wear resistance, except for the composite with kaolin with an aggregate filler content of 2 wt%. Although the friction coefficient in composites with MS is higher than that of the original PTFE, addition of MS had a positive effect on f in comparison with composites containing silicates. It is interesting that a composite containing 1.5 wt.% Kaolin and 0.5 wt.% MS behaves differently than other composites. It also has higher deformation-strength properties which is characteristic of nanocomposites.

To explain the effect of silicates on the physical and mechanical and tribological properties of PCM, studies of the properties and structure of silicates before and after activation were carried out.

There are a lot of data [15-17] on instability of octahedral layers under the mechanical impact. These works show that during the mechanical activation of CC, the Si-O-Me bonds in the octahedral layer are broken while maintaining the oxygen-silicon bonds in the tetrahedral layer. We analyzed water SS extracts and revealed an increase in the number of mobile cations in mechanically activated minerals (Table V). These data are evidence of the release of central cations of the octahedra (Al^{3+} , Mg^{2+}) as a result of the destruction of the octahedral layer in the SS packets. The presence of magnesium cations in kaolin is due to the fact that montmorillonite is included in kaolin.

TABLE V. CONTENT OF MOBILE CAGES OF MAGNESIUM AND ALUMINUM BEFORE AND AFTER MECHANICAL ACTIVATION OF FILLERS

Filler	Cation content, mg / l	
	Mg^{2+} before activation / after activation	Al^{3+} before activation / after activation
Serpentine	6,7 / 22,7	0,035 / 0,024
Kaolin	6,3 / 4,6	1,27 / 4,0
Magnesium spinel	8,55 / 15,06	1,88 / 4,42

Probability of violation of the octahedral SS grid due to the mechanical activation is confirmed by changes in the band of stretching vibrations of the Si – O bonds in the IR spectrum of

serpentine, which indicates force changes in the bonds of the tetrahedral layer (Fig. 1).

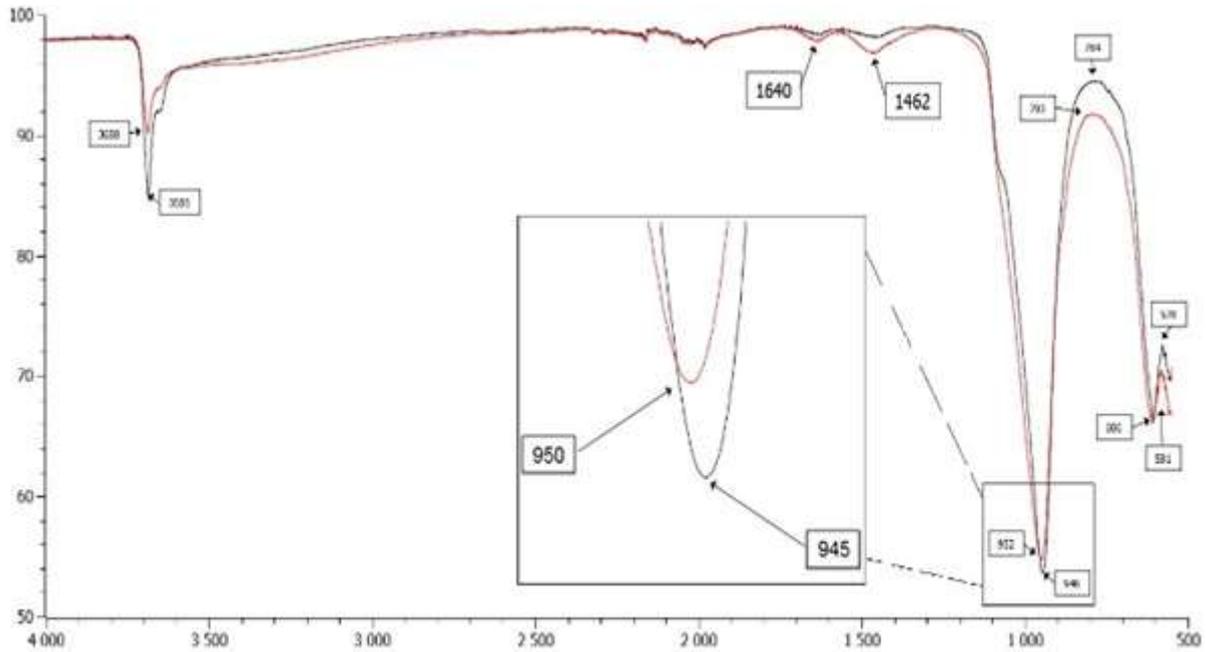


Fig. 1. IR spectra of serpentine before and after mechanical activation.

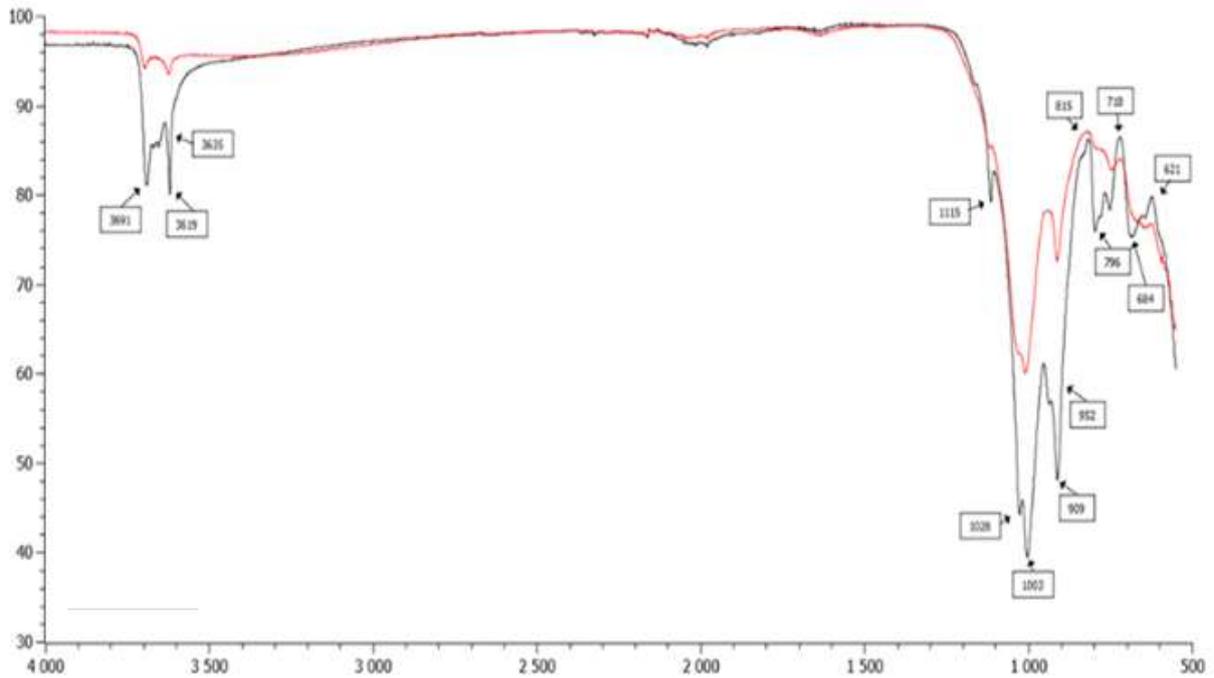


Fig. 2. IR spectra of kaolin before and after mechanical activation

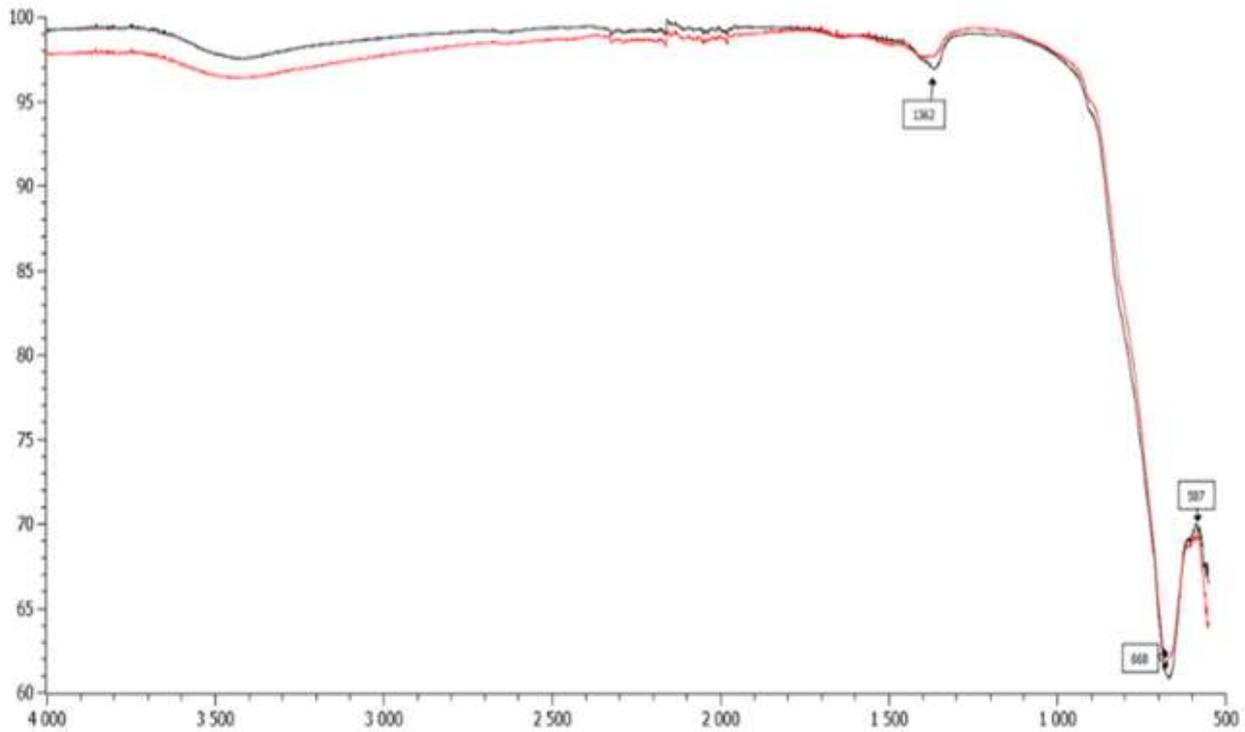


Fig. 3. IR spectra of magnesium spinel before and after mechanical activation.

Figure 1 shows peaks 1640 cm^{-1} and 1462 cm^{-1} . These peaks refer to the carbonate ion bands CO_3^{2-} . These peaks were observed in the initial powder; after mechanical activation they became more intense. According to [15], silicates containing Ca and Mg can absorb carbon dioxide from air during the abrasion process. Since original serpentine was a worn powder, it contained these ions before mechanical activation. During the mechanical activation, absorption of carbon dioxide intensified. Therefore, the peaks in the IR spectra became more intense.

In kaolin (Fig. 2), instead of magnesium, aluminum is present in the octahedral grids. Aluminum does not react with carbon dioxide. Therefore, we did not observe carbonate ion peaks in the IR spectra of kaolin. In the spectra of kaolin, amorphization of the structure of kaolin was observed, since intense crystal peaks had become less pronounced. Distortion of the valence band of Si-O was observed.

As for the IR spectra of magnesium spinel (Fig. 3), no changes in the MS structure were observed after mechanical activation. There were no peaks of carbonate anions.

TABLE VI. CONSTANTS OF STABILITY OF COMPLEX IONS

Central ion / complex	LgK ₁	LgK ₂	LgK ₃	LgK ₄	Lg K ₅	LgK ₆
Al ³⁺ / fluoride(F ⁻)	7.10	11.98	15.83	18.53	20.20	20.67
Mg ⁺² / fluoride (F ⁻)	1.82	-	-	-	-	-

C.Note: The digit of the index under sign K means the number of ligand groups of the central atom of the system dissociated into a given number of steps

The MS structure is close to the densest cubic packing of oxygen whose tetrahedral voids are occupied by Mg^{2+} ions (radius of 0.078 nm), and the octahedral voids – by Al^{3+} ions (radius of 0.057 nm) [17].

MS introduces additional magnesium and aluminum ions into the composite mixture. The chemical activity of magnesium is more pronounced than that of aluminum, but aluminum has a greater ability to form systems. In addition, the ability of aluminum compounds to bind fluorine atoms is widely used in practice [18, 19]. System formation is based on the ability of atoms to form coordination bonds. Aluminum cations having a free orbital are acceptors in relation to fluorine PTFE atoms having three pairs of not divided electrons and oxygen atoms with two pairs of not divided electrons on the SS surface. Data on the stability of complex ions of aluminum and magnesium [20] for compounds with fluorine are presented in Table VI.

V. CONCLUSION

1. Deformation-strength characteristics of composites are enhanced by fillers. The various effects of functional additives on layered silicates were identified.

2. Analysis of the tribotechnical characteristics shows that fillers enhance the wear resistance by 1250 times. The dependence of the wear resistance of composites on the ratio of layered silicates with magnesium spinel was identified.

3. An increase in the amount of central atoms of octahedral silicate networks after mechanical activation was identified. It

speaks for their instability to mechanical effects. This was confirmed by the IR spectroscopy. In addition, formation of carbonate ions during the abrasion of magnesium-containing silicate (serpentine) was identified.

4. The activated NS introduces magnesium and aluminum ions into the mixture. Unlike magnesium cations, aluminum cations have a lower chemical activity, but a higher coordination activity. Due to their coordination ability and exceptional affinity for fluorine atoms, aluminum ions participate in interfacial interaction with the PTFE macromolecule and the surface of the mechanically activated SS, thereby enhancing adhesion interactions at the interface.

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