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Preliminary communications

Practical Advantage of Using WS_2 Nano Coating versus Standard Anti-Corrosion Protection in Industry 4.0

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Abstract: The aim of this paper and research is to obtain real and statistically relevant data that would be an indication of justification of the application of nanotechnology from the aspect of improving the functional properties: anti-corrosive, antifoaming and thermosetting when applying surface protection based on nano particles tungsten disulphide fullerene structure (WS_2) (on metallic materials, coloured materials and alloys), as well as from the aspect of economic cost-effective use of new technologies in Factory of the Future (FoF) and Industry 4.0. The results of the corrosion test show that the WS_2 nanofullerene protection is 72 times higher than the browning layer and is 1.5 times higher than the phosphate layer, with an economically acceptable price-quality ratio (2.5 to 8.8 times more expensive compared to the mentioned protection); since the nano agent, besides anti-corrosion protection, also has anti-wear, antifriction, thermosetting properties.

Keywords: Industry 4.0(I4.0); nano coating; nanocomposites; nanotechnology; WS2 nanofullerene

1 INTRODUCTION

Nanotechnology is a field of science that has been wrapped in secrets for many years and protected from the public's view, because its foundation lies in strictly guarded projects of space and military programs. Basically, it deals with the study and application of various structures of extremely small dimensions (ranging from 10 nm to 100 nm).

Nanoparticles are one of the most common products of nanotechnology and are defined as bodies with a diameter of less than 100 nm. Nanotechnology is as such an ideal basis and one of the key new technologies applied in the development of Industry 4.0.

Due to their specific structure and small dimensions, the nanoparticles are characterized by completely different properties than those of the original materials from which they are made.

In Fig. 1, a comparative comparison of the size of nanoparticles relative to some other known reps can be seen:

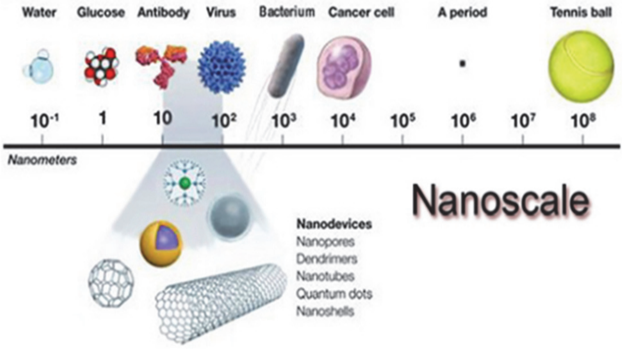

Figure 1 The Nanoscale - Introduction to Nanotechnology [1]

Depending on the desired application effects (depending primarily on their origin and structure), nano layers can be applied to almost all types of surfaces (metal, plastic, lacquered wood, glass, ceramics, textiles, …).

The distribution of nano-composite materials is as follows:

- fullerene,
- nano fibre,
- nano pipes,
- graphene,
- nano particles,
- nano wire,
- quantum dots.

In Fig. 2, you can see the physical appearance of the basic division of materials used for the production of nano composites:

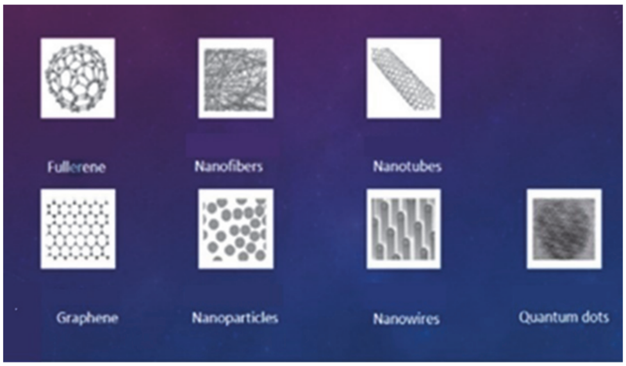

Figure 2 Materials for nano composites

According to [2], for the production of polymer nanocomposites, where the name nanocomposite is used to describe a wide spectrum of materials in which at least one component has submicron dimensions (< 100 nm), nanoparticles of metal (Al, Fe, Au, Ag, ...), oxides (ZnO, Al_2O_3, $CaCO_3$, TiO_2, SiO_2), carbide (SiC), etc., whereby reducing the material size to the nanometre level leads to changes in the optical, thermal, mechanical, electrical and magnetic characteristics of the nanocomposite (depending on which properties of the nanocomposite we want to get it).

Various types of nanoparticles are used to obtain different desired material characteristics. For example, particles based on [3]:

- aluminium nanoparticle (used to obtain material that is characterized by good conductivity),
- silicon carbide - SiC (used to obtain materials with the following characteristics: high strength, hardness and corrosion),
- calcium carbonate (used if we want to achieve a relatively low product cost).

Types of nano composites can be divided into three groups:

- ceramic matrix nano composites (ceramics + TiO_2 + Cu)
  They are distinguished by:
  - high mechanical strength,
  - low coefficient of scratching,
  - high corrosion resistance.
- Polymer-matrix nano composites (polymer matrix + nanoparticles of ceramics, metal, metal sulphides, ...)
  - depending on the type of implanted nanoparticles, the characteristics of the newly created nano composite depend on,
  - better mechanical, antifriction and anti-abrasive properties,
  - better electrical properties.
- Metal-matrix nano composites (metal matrix + carbon nano tubes, tungsten disulfide - WS_2)
  - high tensile force,
  - excellent mechanical characteristics,
  - better electrical conductivity,
  - excellent corrosion resistance.

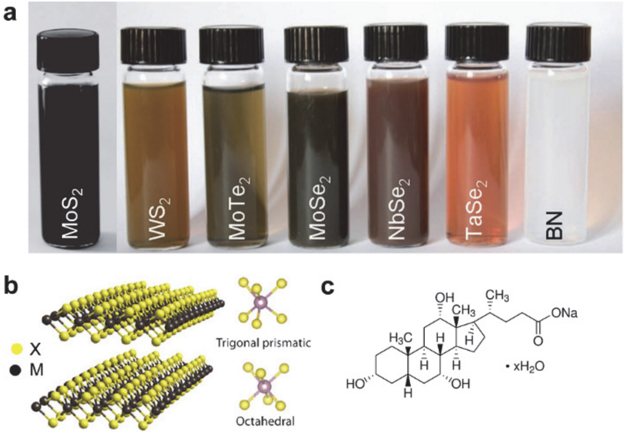

Figure 3 Dispersion of nanosheets of transition metal chalcogenides and BN in aqueous solution requires the use of surfactants such as sodium cholate or SDS. (a) Photograph of dispersions of MoS_2, WS_2, $MoTe_2$, $MoSe_2$, $NbSe_2$, $TaSe_2$, and BN stabilized in water by sodium cholate. The powders were sonicated at initial concentration, **Ci** = 5 mg/ml, with a surfactant of concentration **C(SC)** = 1.5 mg/mL for 30 min; (b) Chemical structure of two layers of a transition metal dichalcogenide where *M* is the transition element and *X* the chalcogen. Two polytypes of single-layers are shown: trigonal prismatic (D_{3h}) and octahedral (D_{3d}); (c) Sodium cholate. (Reproduced with permission from Refs. [4]

In Serbia, at this moment, the only company that deals with the production of nanoparticle-based protective products is "Speedup International d.o.o.", from Belgrade. Nanomaterials that are produced are the most common on the basis of fullerene particles WS_2.

Depending on the base oil and operating conditions, WS_2 nano-fullerenes which are extremely thermal-and pressure-resistant, can reduce the friction coefficient of impregnated surfaces up to 30% using a combination of super-lubricating and surface-treated coating functions.

This is achieved in such a way that the inorganic, "onion-like" multilayered nano-structure of 20-100 concentric WS_2 layers (the diameter range between 30 and 70 nm) reacts to abrasion by exfoliating thin outer layers of particles that cover the surfaces with the continuous layer of the dual effect lubricant.

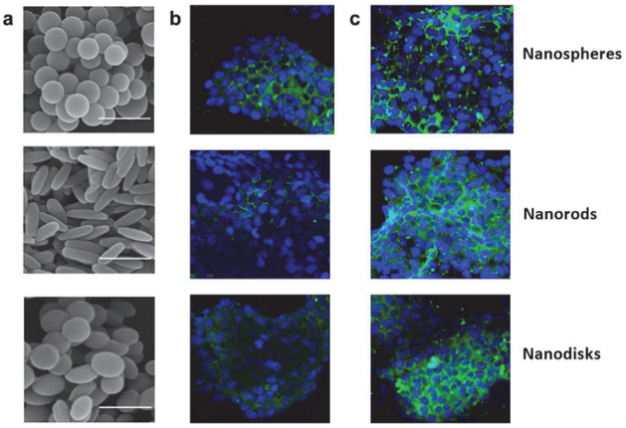

Figure 4 Polymer nanoparticle shape and surface properties are critical parameters for drug release. (a) Nanospheres, rods, and discs (Scale bar: 500 nm); (b) Confocal micrographs of nanoparticle uptake in breast cancer cells without trastuzumab protein coating; (c) Increased nanoparticle uptake with trastuzumab protein coating. Microparticles of different size (above 1 μm) of the same shapes were also tested and found to exhibit different uptake characteristics. [4]

Due to these layered structures of nanofullerene particles, WS_2-based agents have great anti-friction and anti-wear characteristics. These characteristics allow the repair of damage in the form of micro-cuts (or erosion resulting from exploitation), using and combining different nanotechnology-based agents and processes (with the application of different thickness of nano-agent layers).

2 METHODS

We used the standard experimental method and the toughest procedure for corrosion testing, standard JAS 0 270, METHOD 107, REGIME C.

2.1 Experimental

In this experiment has been tested the comparative behaviour of 3 different types of anti-corrosive surface protection at 4 different parts made of structural steel.

Types of anti-corrosive surface protection:

1. Browning layer,
2. The phosphate layer,
3. Nano protection (WS_2 nanofullerene structure).

Type of test material: structural steel (Steel grades: 25CrMo4, Number: 1.7218)

Total number of tested pieces: 36 pcs (3 pcs for each type of surface protection per position).

The duration time for testing procedures: 7 days.

2.2 Preparation of External and Internal Surfaces of Materials for Anticorrosion Surface Protection

Preparation of parts for surface protection is a very important factor. Fig. 5 shows an automated grinding plant and the preparation of metal surfaces for applying surface protection, while Fig. 6 shows the appearance of the parts after the final preparation for application of the protection.

2.3 Nano Coating Procedure

The procedure of programming the CNC machine for applying nano coating is done by us in strictly controlled environment friendly conditions (temperature, pressure, machine speed, inclination) using the nano coating on WS_2 basis.

Figure 5 Display of the machine for the machine removal of metal coatings and the collection of parts for application of surface protection

Figure 6 Rotamat R90C nano coating machine

Figure 7 Display of parts during application of nano coating in the Rotamat R90C machine

CNC machine programming is done because of the repeatability of the process. When a technological process for a particular position is won, that technology remains permanently recorded in the memory of the machine for later use. As many times as necessary to do the serial production of nano protection for a particular position, the procedure and results obtained are always the same. The advantage is that after "conquering" a technological process for a certain position, the presence of a technologist engineer is no longer required in exploitation, but it is sufficient that only a technician is present for manipulation.

2.4 Testing Procedure

The test is carried out to verify the correctness of the function and resistance of the agent in salt fog conditions, as well as to gain insight into the uniformity of the quality of the corrosion protection of the substances being tested. In Fig. 9, the prepared parts can be seen before the start of the test in the saline fog chamber.

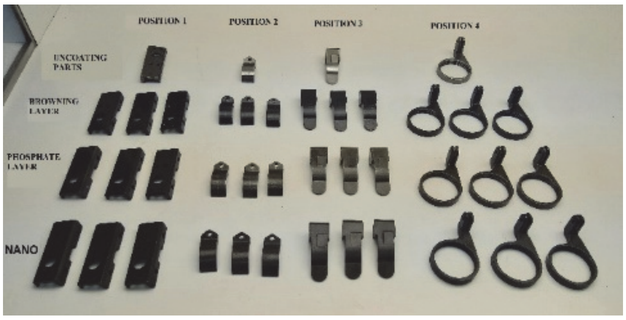

Figure 8 Display of parts before testing and placing in a saline fog chamber

After selecting the austerity regime (in our case it was the strictest regime of corrosion testing), the agents were placed in the chamber and the testing began.

A 5% solution of sodium chloride (NaCl p.a.) for testing was made and processed according to these regulations:

- pH of saline solution: 6.5,
- Salt fog concentration: 1.6 cm^3/h.

The spraying lasts for two hours, after which the products are taken from the saline fog chamber and stored in a device with a temperature of 35 ± 2 °C and a relative humidity of 90 to 95% over a period of 22 hours.

After the end of the cycle, the agents were examined and tested for corrosion while still moist from saline fog (or after rinsing and drying).

The entire procedure and test procedure were repeated for the next 7 days.

In the pictures from the regular number from 10 to the number 18, the entire test procedure can be visually seen, as well as the test results themselves.

Figure 9 Display of treated parts during the testing in a saline fog chamber

Figure 10 Display of parts after the 7 days testing in a saline fog chamber

Process parameters:

- Charger quantity:
  - Without filler (position 4)
  - With filler: m = 1 - 1.2 kg (positions 1, 2, 3)
- Material pressure: p = 0.06 - 0.12 bar
- Material temperature: T = 30 - 50 °C
- Drum speed: V = 2 rpm
- Drum angle: 37 °
- Amount of protective agent: 250 - 380 gr
- Number of cycles: 8-10
- Cycle duration:
  - Spray gun: t = 30 - 60 sec
  - Drying: t = 3 - 5 min.

3 RESULTS

In the examinations shown below, we can see the results of comparative laboratory testing of surface protection (browning layer, phosphate layer and nano coating) with required and established values.

3.1 Examination

- **DAY 1** (Beginning of testing)

About 1h after testing, we do not have any trace of corrosion on parts and all coatings meet the requirements.

The next testing was performed 2 hours after the start of the examination and the following results were obtained. The corrosive changes were observed on the browning layer coating, but there were not observed traces of corrosion on phosphate layer coatings and nano coating.

- **DAY 2** (Results after 24 h of testing)

After 24h of testing, at browning layer was observed corrosion at all parts. On the other hand, no trace of corrosion was observed on the parts treated with phosphate layer coatings and nano coating.

- **DAY 3** (Results after 48 h of testing)

After 48 h of testing, at browning layer was observed corrosion at all parts and trace of corrosion at parts treated with phosphate layer. On the other hand, there were no corrosion marks at parts treated with nano coating.

- **DAY 4** (Results after 72 h of testing)

After 72 h of testing, corrosion was observed at all parts treated with browning layer and phosphate layer. On the other hand, a slight corrosion trace was observed on position 3 (parts treated with nano coating).

- **DAY 5** (Results after 96 h of testing)

After 96 h of testing, corrosion was observed at all parts treated with browning layer and phosphate layer. On the other hand, traces of corrosion were detected on position 2 and position 3, which were treated with nano coating.

- **DAY 6** (Results after 120 h of testing)

After 96 h of testing, corrosion was observed at all parts treated with browning layer and phosphate layer. On the other hand, at parts which were treated with nano coatings corrosion was detected (on the positions 2 and 3), and at these parts was also noticed the removing of the coating on the edges.

- **DAY 7** (Results after 144 h of testing)

After 144 h of testing, corrosion was observed at all parts treated with browning layer and phosphate layer. On the other hand, at parts which were treated with nano coatings, spot corrosion was observed and removed coating on edges at all pieces, but at positions 1 and 4 traces of spot corrosion were observed.

All results of testing 4 different types of anticorrosion protection could be seen in the following Figs. 11 to 17, where the level of corrosion is marked as:

0 - No corrosion
1 - Traces of spot corrosion
2 - Full corrosion.

1 Day				
Type of anti corrosion protection	Position 1	Position 2	Position 3	Position 4
Browning layer	2	2	2	2
Phospate layer	0	0	0	0
NANO coating	0	0	0	0

Figure 11 Results of anti corrosion testing after 1day in salt chamber

2. Day				
Type of anti corrosion protection	Position 1	Position 2	Position 3	Position 4
Browning layer	2	2	2	2
Phospate layer	0	0	0	0
NANO coating	0	0	0	0

Figure 12 Results of anti corrosion testing after 2 days in salt chamber

3. Day				
Type of anti corrosion protection	Position 1	Position 2	Position 3	Position 4
Browning layer	2	2	2	2
Phospate layer	1	1	1	1
NANO coating	0	0	0	0

Figure 13 Results of anti-corrosion testing after 3 days in salt chamber

4. Day				
Type of anti corrosion protection	Position 1	Position 2	Position 3	Position 4
Browning layer	2	2	2	2
Phospate layer	2	2	2	2
NANO coating	0	0	1	0

Figure 14 Results of anti-corrosion testing after 4 days in salt chamber

5. Day				
Type of anti corrosion protection	Position 1	Position 2	Position 3	Position 4
Browning layer	2	2	2	2
Phospate layer	2	2	2	2
NANO coating	0	1	1	0

Figure 15 Results of anti-corrosion testing after 5 days in salt chamber

6. Day				
Type of anti corrosion protection	**Position 1**	**Position 2**	**Position 3**	**Position 4**
Browning layer	**2**	**2**	**2**	**2**
Phospate layer	**2**	**2**	**2**	**2**
NANO coating	**0**	**2**	**2**	**0**

Figure 16 Results of anti-corrosion testing after 6 days in salt chamber

7. Day				
Type of anti corrosion protection	**Position 1**	**Position 2**	**Position 3**	**Position 4**
Browning layer	**2**	**2**	**2**	**2**
Phospate layer	**2**	**2**	**2**	**2**
NANO coating	**1**	**2**	**2**	**1**

Figure 17 Results of anti-corrosion testing after 7days in salt chamber

4 DISCUSSION

The results of concurrent testing show that when using the same material (structural steel for testing all 4 positions) and the same test conditions, nano surface protection on the basis of WS2 is 6 times more durable than the browning layer, and 2 times more durable than the protection of the phosphate layer.

All parts were protected with a thin layer of protective oil before the corrosion testing according to the standard, which additionally increased the anticorrosion protection.

The thickness of the applied protective layer on the parts treated with nano coating was everywhere uniform and ranged from 5 to 15 microns.

The thickness and formulation of the protective layer at parts depends directly on the geometry of the parts themselves.

If the parts have a complex geometric shape and sharp edges, it is more complex to make the appropriate protective formulation and nano coating technology.

Comparing the obtained results with the usual results of the corrosion test on steel according to the standard JAS 0 270, METHOD 107, REGIME C, where it can be stated that the beginning of corrosion on steel parts protected by the browning layer occurs after testing for 2 hours in saline solution (or for 1 hour in saline), while on the phosphate-protected photovoltaic steel coatings after 4 hours of salt solution (or 2 hours in saline chamber), it can be clearly seen that the standard types of surface protection (browning layer and phosphate layer) do not deviate from the results of the above values, more precisely, they are confirming the standard.

A comparative techno-economic analysis (which can be seen in Tab. 1 and Tab. 2) says that the ratio of cost-quality protection is far on the side of newly developed WS_2 based nano protection (fullerene structure) compared to the existing standard methods (minimum 72 times better anti-corrosion protection than brunir and minimum 1,75 times better anti-corrosion protection than phosphate layer); especially when taking into account the fact that the nano protection is not only anti-corrosive in itself, but also has other very important characteristics (anti-abrasive, antifriction, temperature-resistant, with the characteristic of drastic reduction in light reflection of the work).

Table 1 Comparative techno-economic analysis of the quality of surface protection 1

Comparative techno-economic analysis of the quality of surface protection							
No	Position	Quality of surface protection -Time to the appearance of corrosion- [h]					
		Browning layer		Phosphat Layer		WS2 nano coating	
		Spot corrosion	Total corrosion	Spot corrosion	Total corrosion	Spot corrosion	Total corrosion
1	Position 1	-	2	72	96	96	144
2	Position 2	-	2	72	96	120	144
3	Position 3	-	2	72	96	168	-
4	Position 4	-	2	72	96	168	-

Table 2 Comparative techno-economic analysis of the quality of surface protection 2

Comparative techno-economic analysis of the quality of surface protection			
No	**Position**	**WS2 nano anti corrosion improvement comparisation**	
		Browning layer	**Phosphat layer**
1	**Position 1**	**144 h / 2 h = 72**	**144 h / 96 h = 1.5**
2	**Position 2**	**144 h / 2 h = 72**	**144 h / 96 h = 1.5**
3	**Position 3**	**168 h / 2 h = 84**	**168 h / 96 h = 1.75**
4	**Position 4**	**168 h / 2 h = 84**	**168 h / 96 h = 1.75**

Tab. 3 also shows that the cost of surface protection for browning layer and phosphate layer is the same, while nano protection is 5 to 8.8 times more expensive compared to the above.

Table 3 Comparative techno-economic analysis of the quality of surface protection 3

Comparative techno-economic analysis of the quality of surface protection				
No	**Position**	**Anticorosion price comparison**		
		Browning layer	**Phosphat layer**	**WS2 nano coating**
1	**Position 1**	**1**	**1**	**2.78**
2	**Position 2**	**1**	**1**	**5.98**
3	**Position 3**	**1**	**1**	**8.8**
4	**Position 4**	**1**	**1**	**2.5**

The tables below (Tab. 4, Tab. 5 and Tab. 6) show comparative techno-economic analysis of the prices of standard surface protection procedures and how to get comparative calculations of the anti-corrosion coating prices.

Table 4 Comparative techno-economic analysis of the prices of the standard procedures of surface protection

No	**Position**	**Weight of one piece [kg/pcs]**	**Browning layer price [EUR/kg]**	**Phosphat layer price [EUR/kg]**	**WS2 nano coating price [EUR/Liter]**	**Number of treated nano-coating [pcs]**	**Quantity of used nano materials [Liter]**
1	Position 1	W1	A	**B=A**	C	N1	Q1
2	Position 2	W2				N2	Q2
3	Position 3	W3				N3	Q3
4	Position 4	W4				N4	Q4

Table 5 Comparative techno-economic analysis of the prices of the standard procedures of surface protection

No	Position	Anti-corrosion Coating Price		
		Browning layer price [EUR/pcs]	Phosphat layer price [EUR/pcs]	WS2 nano coating price [EUR/pcs]
1	Position 1	B1=A/W1	P1=B/W1	N1=C/W1
2	Position 2	B2=A/W2	P2=B/W2	N2=C/W2
3	Position 3	B3=A/W3	P3=B/W3	N3=C/W3
4	Position 4	B4=A/W4	P4=B/W4	N4=C/W4

Table 6 Comparative techno-economic analysis of the prices of the standard procedures of surface protection

No	Position	Anti-corrosion Price Comparison		
		Browning layer price	Phosphat layer price	WS2 nano coating price
1	Position 1	BLP1=B1/P1=**1**	PLP1=P1/B1=**1**	WNCP1= N1/P1=**2.78**
2	Position 2	BLP2=B2/P2=**1**	PLP2=P2/B2=**1**	WNCP2= N2/P2=**5.98**
3	Position 3	BLP3=B3/P3=**1**	PLP3=P3/B3=**1**	WNCP3=N3/P3=**8.8**
4	Position 4	BLP4=B4/P4=**1**	PLP4=P4/B4=**1**	WNCP4=N4/P4=**2.5**

According to all mentioned, use of this procedure in relation to the existing methods has fully justified the expectations.

5 CONCLUSIONS

Transition to the upcoming new Industrial revolution known as Industry 4.0 will necessitate that those who are currently working in the industry acquire the significant appropriate knowledge and skills to introduce new technologies and processes (concentrations of technical expertise and know-how with respect to Industry 4.0), which they currently do not have.

The need to develop and implement the new modern leading-edge technologies is a key factor to ensure the development of products and the only way to be able to compete with international rivals and attract foreign customers.

Related to Industry 4.0, among one of the most defining technology trends are benefits of using advanced materials (nanotechnology). Products based on nanotechnology have a wide area of application in different industries (aerospace, automotive, defense, construction, health, etc.).

Advanced materials and nanotechnology have been identified as a priority area in the majority of EU Member States [5].

When we are speaking of nano composites, the basic conclusion that can be performed is that they, although having up to 10 times less active particles than ordinary composites, generally have better thermal, mechanical, electrical and chemical characteristics, and can cover all areas of industrial applications depending on their composition and structure.

Also, nano coatings inhibit corrosion several times better than the standard procedure, decrease friction and increase wear protection and durability.

In conclusion, we can say that even though a lot has been done today in the area of anti-corrosive surface treatment with standard procedures, in the future there is a lot of space for technological advancements in the area of nano-technology and nano coatings.

The obtained results of this test are only indicative of this fact.

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