

Robotic Submerged Microhandling Controlled by pH switching

Jérôme Dejeu, Patrick Rougeot, Michaël Gauthier and Wilfrid Boireau

Abstract—Robotic microhandling is a promising way to assemble microcomponents in order to manufacture new generation of Hybrid Micro ElectroMechanical Systems (HMES). However, at the scale of several micrometers, adhesion phenomenon highly perturbs the micro-objects release and the positioning. This phenomenon is directly linked to both the object and the gripper surface chemical composition. We propose to control adhesion by using chemical self-assembly monolayer (SAM) on both surfaces. Different types of chemical functionalisation have been tested and this paper only focuses on the presentation of aminosilane grafted (3 (ethoxydimethylsilyl) propyl amine (APTES) and (3 aminopropyl) triethoxysilane (APDMES)). We show that the liquid pH can be used to modify the adhesion and to switch from an attractive behaviour to a repulsive behaviour. The pH control can thus be used to increase adhesion during handling and cancel adhesion during release. Experiments have shown that the pH control is able to control the release of a micro-object. This paper shows the relevance of a new type of reliable submerged robotic microhandling principle, which is based on adjusting chemical properties of liquid.

I. INTRODUCTION

Manufactured products are getting smaller and smaller and integrate more and more functionalities in small volumes. Several application fields are concerned such as telephony, bio-engineering, telecommunications or more generally speaking the Micro-Electro-Mechanical-Systems (MEMS). The assembly of these microproducts is a great challenge because of the microscopic size of the components. In fact, the major difficulty of micro-assembly comes from the particularity of the micro-objects behaviour which depends on surface forces [1], [2], [3]. The manipulation of a micro-object requires handling, positioning, and releasing it without disturbances of the surface forces such as electrostatic forces, van der Waals forces or capillary forces. The release is the most critical phase which is usually hindered by adhesion [4], [5].

Several methods have been proposed in the last ten years to improve micromanipulation [6], [7]. The first approach consists in using non-contact manipulation like laser trapping [8] or dielectrophoresis [9]. These manipulation methods are not disturbed by adhesion but the related blocking

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forces stay low, which is a major drawback when applied in microassembly. The second approach deals with contact manipulation where the adhesion is reduced or directly used for manipulation. The reduction of the adhesion can be achieved for example by raising the roughness of the end-effectors [10], [11]. Adhesion can be directly used to perform manipulation tasks. In this case, one-fingered gripper is sufficient to handle objects, but a releasing stays difficult [12]. In fact, new methods are required such as inertial [13] or dielectrophoresis release [14]. The major advantage of contact handling consists in the fact that the blocking force is usually high. The current microhandling methods are able to improve micromanipulation but the object behaviour is always disturbed by adhesion and the reliability is still low [11], [15]. Different methods were proposed, in the last ten years, to improve microhandling by chemical functionalisation of the micro-object as the adsorption of the hydrophobic alkanethiol [16] or hydrophobic (16-Mercapto)hexadecanoic acid [17]. The latter compound can switch the surface property from hydrophobic to hydrophilic by modification of the electrical potential.

We propose a new contact handling system that chemically contrast the surface forces between the object and the gripper [18]. The major objective is to control the adhesion force or to create a repulsive force to guarantee a reliable release. Now, the surface properties of a material can be controlled by surface functionalisation in a liquid by modifying the pH. The charge density on functionalized surfaces is effectively linked to the pH.

The microhandling principle is presented in figure 1. The grasping can be done at pH_1 where the surface charge on the gripper and the object induces an attractive force. In order to release the object, the pH is modified to a second value pH_2 where the object charge is changing. The electrostatic force becomes repulsive and the object is released.

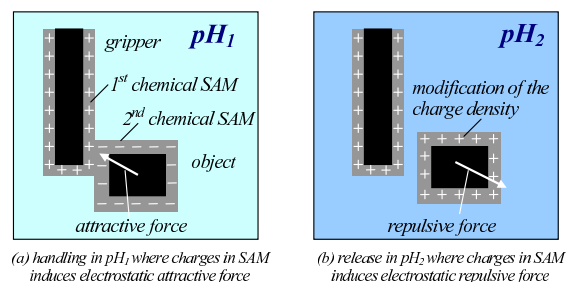


Fig. 1. Principle of the Robotic Microhandling controlled by Chemical Self Assembly Monolayer (SAM)

The microhandling method proposed is based on two chemical functions: amine and silica (see in figure 2). In one hand, the amine group is in the state NH_2 in basic pH and in NH_3^+ in acidic pH. In the other hand, the silica surface charge in water is naturally negative, excepted for very acidic pH, where the surface is weakly positive [19].

	amine function	hydroxyl groups on silica
acidic pH	$-NH_3^+$	Si(OH)
basic pH	$-NH_2$	SiO $^-$

} protonation

Fig. 2. Modification of the electrical charges on chemical elements in function of the pH type

The objective of this article consists in showing the relevance of pH use control submerged microhandling. The surface chemical functionalizations are presented in the following section. Section III deals with interaction force measurement between functionalized surfaces in liquid depending on the pH. A model of interaction force and discussions on force measuring are proposed in section IV. In the last section, pH controlled experimental micromanipulation tasks are presented.

II. CHEMICAL FUNCTIONALISATION

A. General principles

The surface functionalisation of both object and gripper can be obtained by different methods. The two most important methods are the polyelectrolytes physisorption (polyelectrolyte with positive or negative charges) [20], [21] or the molecules grafting on the surface (covalent bond between the substrate and the molecules) [22], [23].

We chose to investigate the second method because, firstly, it generates covalent bond between substrate and molecules. These molecules must contain silanol, thiol, azide, allyl or vinyl groups [22], [23] in one extremity. These molecules have to be used in organic solvent such as toluene, acetone, methanol, ethanol, etc. The silanol creates a Si-O-Si bond with the silica substrate [22] while allyl or vinyl generates Si-O-C (or Si-C) bond [24] and the azide groups produce Si-N bond [25]. The second reason is that the layer created by silanisation did not exhibit any signature of degradation when stored in an airtight container for 18 months [26], and was stable up to a temperature near of 350°C [27], [28] even when washed using 1% detergent solution, hot tap water or organic solvents and aqueous acid at room temperature [27]. This silane layer was robust under the same daunting conditions that all existing semiconductor materials already endure such as thermal stability up to 350°C, chemical stability under different etchants. So the functionalised MEMS can be used in molecular and/or hybrid electronics.

B. Materials and chemicals

Two chemical functionalisations have been tested (see in figure 3):

- the silane, 3 (ethoxydimethylsilyl) propyl amine (APTES);
- the silane, (3 aminopropyl) triethoxysilane (APDMES).

Both chemical compounds (APTES, APDMES) used to surface functionalisation are amine functions NH_2 which can be protonated or ionised to NH_3^+ according to pH. In acidic pH, the amine is totally ionised, then the ionisation decreases and is null in basic pH (between pH 9 and 12). The silanes (APTES and APDMES), ethanol, sodium chloride (NaCl), sodium hydroxyde (NaOH) and chlorydric acid (HCl), were purchased from Sigma Aldrich.

The deposits were made on silicon surfaces. The Milli Q water (deionisation and then ultrafiltration of the water) was obtained with the Direct-Q 3 of Millipore. The solution pH was measured with a pH-meter (Sartorius, PT-10) and an electrode (Sartorius, PY-P22), and adjusted with addition of sodium hydroxyde and chlorydric acid just before measurement.

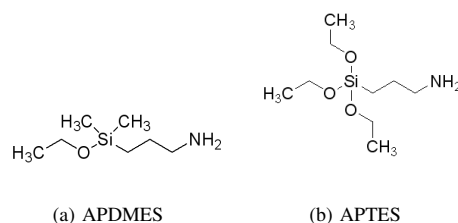


Fig. 3. Molecules used for the silica functionalisation.

C. Surface functionalisations

Before being functionalised, the wafers were cleaned by immersion in a piranha solution (2 parts H_2SO_4 , 1 part H_2O_2) during 25 minutes at 70°C. Then, the wafer were rinsed, stored in Milli Q water before PAH functionalisation or rinsed in milli Q water and in ethanol before silanisation (functionalisation by silane: APDMES, APTES). Solutions were freshly prepared by direct dissolution in milli-Q quality water and in ethanol for respectively the PAH and the silanes. The final silanes concentration was 1%. The surfaces were functionalised by immersion in solutions during one night at room temperature. In the silanes solution, the molecules were grafted on the substrate (covalent bond). The excess of ungrafted silanes was removed by ultrasonication during 2 minutes in ethanol.

D. Functionalisation mechanisms: Grafted silanes

The self assembled monolayers formation mechanism during silanization process takes place in four steps [26]. The first step is physisorption, in which the silane molecules get physisorbed at the hydrated silicon surface. In the second

step, the silane head-groups arrive close to the substrate hydrolyse, in the presence of the adsorbed water layer on the surface, into highly polar hydroxysilane $-\text{Si}(\text{OH})$. These polar $\text{Si}(\text{OH})$ groups form covalent bonds with the hydroxyl groups on SiO_2 surface (third step). During initial period, only a few molecules will adsorb (by steps 1-3) on the surface and the monolayer will definitely be in a disordered (or liquid) state. However, at long term, the surface coverage eventually reaches the point where a well-ordered and compact (or crystalline) monolayer is obtained (step 4). This step applies only for APTES, by the condensation reaction between the APTES molecules.

III. EXPERIMENTAL FORCE MEASUREMENTS

A. Atomic Force Microscope

Force measurements were performed in order to characterize the functionalisations. Force-distance curves were performed using a stand-alone SMENA scanning probe microscope (NT-MDT). The force measurement performed on this Atomic Force Microscope (AFM) is based on the measurement of the deformation of the AFM cantilever with a laser deflection sensor. The silicon rectangular AFM cantilever, whose stiffness is 0.3N/m , was fixed and the substrate moved vertically. As the applicative objective of this work is to improve reliability of micro-object manipulation, interactions have been studied between a *micrometric* sphere and a plane. Measurements were in fact performed with a cantilever where a borosilicate sphere ($r_2 = 5\mu\text{m}$ radius) was glued (Ref.: *PT.BORO.SI.10*, company Novascan Technologies, Ames, USA). All measurements were done at the driving speed of 200 nm/s to avoid the influence of the hydrodynamic drag forces [29]. For each sample, nine measures were done in different points. The repeatability of all the pull-off and pull-in forces values was better than 10 %.

B. Typical distance-forces curves

The first type of behaviour is presented in figure 4. In this case, an attractive force (pull-in force) is measured when the sphere is coming close to the substrate (near -20 nN , figure 4). In figure 4, we clearly measured a pull-off force which represents the adhesion between the borosilicate sphere on the tip and the functionalised substrate. In this example, the pull-off force is reaching $-1.1\ \mu\text{N}$. This behaviour represents an attraction between surfaces.

The second type of behaviour is presented in figure 5. In this case, there are repulsion between surfaces. We observe a repulsion (positive pull-in force near $0.75\ \mu\text{N}$) and no pull-off force between both surfaces.

C. Influence of the pH on the interaction

Experiments have been done in wet medium with the functionalised surface and

- a cantilever grafted with APTES or
- a non-functionalised cantilever.

The pH of the solution varied by addition of sodium hydroxide or chlorhydric acid. The surface rested in the

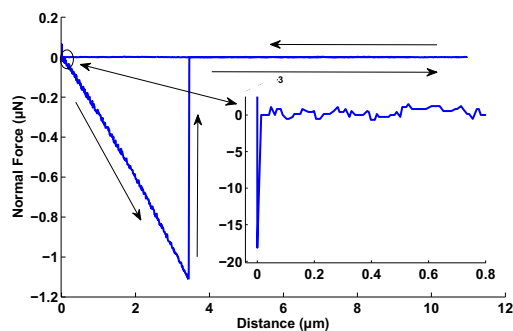


Fig. 4. Force-distance curves on functionalised APTES in dry medium (spring constant 0.3 N/m).

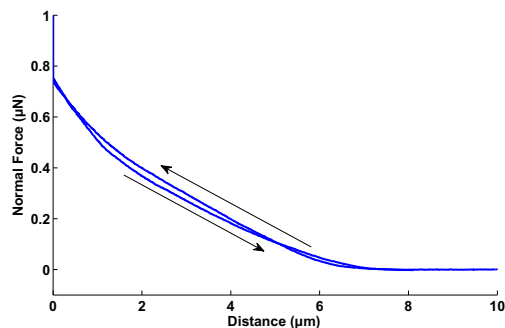


Fig. 5. Force-distance curve for the APDMES functionalised substrate in wet medium (spring constant 0.3 N/m).

solution for 2 minutes before the measurement, in order to equilibrate the system. Force measurement in liquid has been also compared with measurement done in air.

1) *Functionalised surface*: First, the measurements were done with a cantilever and a non-functionalised sphere. The results of the pull-in and pull-off forces are presented in figure 6.

In this figure, we noted that the pH influences significantly the forces between the cantilever and the surface. At natural pH, an attractive pull-in is measured (near -60 nN , Figure 6(a)) with an important pull-off (-350 nN , Figure 6(b)). When the pH increases the pull-in force is inverted and becomes repulsive respectively 280 nN and 770 nN at pH 9 and 12. Moreover, the adhesion forces disappear. The average values of the different measurements, (pull-in and pull-off forces), at different pH, are summarized in the table I.

In this table, we observe that the phenomena described above for APTES is the same for APDMES. In fact at natural pH (near 5.5), the interaction is attractive with an important adhesion force and at basic pH, above 9, the interaction is repulsive. At pH 2, we do not detect pull-in force probably because the charge density on the silica cantilever was too low. In this table, we shown that the forces measured with APDMES grafted are lower than APTES. We can explain this by the fact that the quantity

of molecules grafted on the substrate is more important for APTES than APDMES.

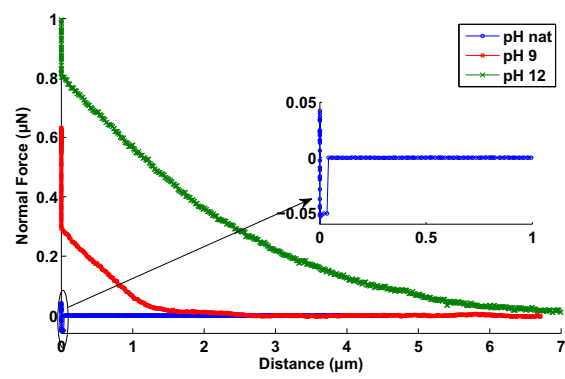
As the charges on the surface of the silica cantilever are negative or null (see figure 2), the surface density σ of APTES and APDMES verifies:

$$\begin{aligned} &\text{for pH nat or 2, } \sigma \geq 0 \\ &\text{for pH 9 or 12, } \sigma \leq 0. \end{aligned} \quad (1)$$

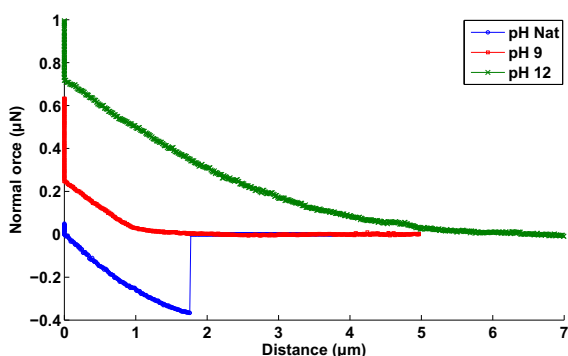
In fact, in acid pH, the positive charges induced by the functionalisation are greater the negative charges induced by the hydroxyl groups. In basic pH, the negative charges are predominant.

The inversion of the interaction forces during the variation of the pH of the solution represents a great interest in micromanipulation. The control of the pH is in fact able to switch from an attractive behaviour (grasping) to a repulsive behaviour (release).

2) *Functionalised surface and cantilever:* Secondly, the cantilever was functionalised with the APTES silane and without sonification step. Similar experiments as previous were performed in aqueous solution of pH that varied between 2 and 12. The force-distance curves obtained with a APDMES grafted on the substrate are presented in figure 7.



(a) Approach measurement



(b) Retract measurement

Fig. 6. Force-distance curve for the APTES functionalised substrate in wet medium at different pH (spring constant 0.3 N/m).

TABLE I

INFLUENCE OF THE pH ON THE PULL-IN AND PULL-OFF FORCES (SPRING CONSTANT 0.3 N/M) FOR APTES AND APDMES GRAFTED ON THE SURFACE.

Medium	APTES		APDMES	
	Pull-in (nN)	Pull-off (nN)	Pull-in (nN)	Pull-off (nN)
pH 2	0	-176	0	-93
pH nat	-59.5	-387	-29.8	-353
pH 9	282	0	377	0
pH 12	768	0	1100	0
Air	-13.2	-1150	-4.97	-769

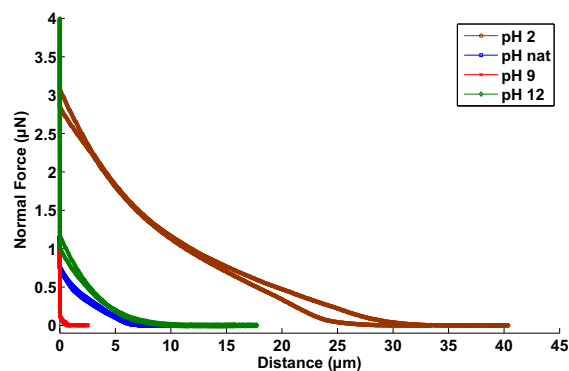


Fig. 7. Force-distance curve for the APDMES functionalised substrate in wet medium at different pH obtained with a tip functionalised APTES (spring constant 0.3 N/m).

Contrary to the case in the air, the forces measured in the liquid were always repulsive between the functionalised cantilever with APTES and the APDMES grafted on the surface. We did not detect any pull-off force. There was in fact no adhesion between both functionalised objects. A cantilever deformation was observed on an important distance (typically several microns) when the sphere is approaching from the surface. This large interaction distance typically comes from electrostatic interactions. The average values of the force measurements at different pH, are summarized in the table II.

TABLE II

INFLUENCE OF THE pH ON THE PULL-IN AND PULL-OFF FORCES (nN) OBTAINED WITH A TIP FUNCTIONALISED APTES (SPRING CONSTANT 0.3 N/M) FOR APTES AND APDMES GRAFTED ON THE SURFACE.

Medium	APTES		APDMES	
	Pull-in (nN)	Pull-off (nN)	Pull-in (nN)	Pull-off (nN)
pH 2	3190	0	3080	0
pH nat	655	0	735	0
pH 9	150	0	114	0
pH 12	983	0	989	0
Air	0	-91	0	-136

In this table, we note that the pH of the medium changes the value of the repulsive force between the cantilever and the surface but the behaviour stays always repulsive. For acidic and natural pH, the repulsion can be explained by the positive charges of the aminosilane grafted on the surface. For basic pH, repulsion is induced by the negative charges of the silicon substrate down to the functionalisation. Indeed, from pH 9, the positive charge of the aminosilane are not sufficient to totally screening the negative charge of the silicon. However at pH 9, the charge screening induced by some NH_3^+ explains why the repulsion are lower with a functionalised cantilever (pH 9 in Table II) than with a non-functionalised cantilever (pH 9 in Table I). Moreover, at pH 12, behaviour of the functionalised surface and the non-functionalised surface are quite similar. In fact, the aminosilane has any positive charges left and the repulsion is only induced by the negative charge on silicon and borosilicate.

In micromanipulation, the repulsive charge between two objects is an interesting behaviour in order to make easier the separation of two objects whatever the pH of the solution,. Indeed, the release of micro-objects will be easier if both micro-object and gripper is functionalised with aminosilane which induces repulsive force.

IV. MODELING OF THE SURFACE CHARGES

In order to be able to extrapolate this result to other geometries, the electrical surface density induced by the functionalisation have been studied. Based on the force measurements, the surface charges on the substrate could be estimated. We assume that the surface is large enough to be considered as infinite compared to the sphere whose radius is $r_2 = 5 \mu m$. The electric field E_1 induced by the surface charge density σ_1 of the substrate is uniform:

$$\vec{E}_1 = \frac{\sigma_1}{2\epsilon_3\epsilon_0} \vec{n}_1 \quad (2)$$

where ϵ_0 is the electric permittivity of the vacuum and ϵ_3 the relative permittivity of the medium (for water, $\epsilon_3=80$), \vec{n}_1 unit vector perpendicular to the substrate. The repulsive electrostatic force applied by the gripper on the object whose charge is q_2 is thus:

$$\vec{F}_{pull-in} = q_2 \cdot \vec{E}_1 = 2\pi r_2^2 \frac{\sigma_1 \sigma_2}{\epsilon_3 \epsilon_0} \vec{n}_1 \quad (3)$$

where σ_2 is the charge density on the sphere whose radius is r_2 .

If both objects have the same surface density σ_1 , this later can be deduced from the force measurement:

$$|\sigma_1| = \left(F_{pull-in} \frac{1}{2\pi r_2^2} \frac{\epsilon_3 \epsilon_0}{\sigma_1} \right)^{\frac{1}{2}} \quad (4)$$

The sign of σ_1 should be determined by considering the chemical functions (equations (1)). The equation (4) has been used to determine the charge density of APTES (see in table III). Moreover, in case of an interaction between two different functionalised surfaces, the charge density σ_2 of the second surface is done by:

$$\sigma_2 = \frac{F_{pull-in} \frac{1}{2\pi r_2^2} \epsilon_3 \epsilon_0}{\sigma_1} \quad (5)$$

This equation (5) has been used to determine the electrical surface density of APDMES (see in table III).

TABLE III

ELECTRICAL SURFACE DENSITY OF THE FUNCTIONALISED SURFACE IN FUNCTION OF THE pH

pH	APTES	APDMES
	$\sigma_1 (\mu C/cm^2)$	$\sigma_2 (\mu C/cm^2)$
pH 2	+0,38	+0,36
pH nat	+0,17	+0,19
pH 9	-0,08	-0,06
pH 12	-0,21	-0,21

In this table, the sign of the charge density was that determined in section III-C-2. Buron et al. are also found a positive charge density at pH natural (5.5) [30]. The value of the charge density was weak (less than $1 \mu C/cm^2$), so grafted amino groups density was about 0.2 sites/nm² and 1% of silanol group was grafted by silane. This value can be explain by the important influence of the grafted condition and more particularly of the water content in the solution and in the atmosphere [31].

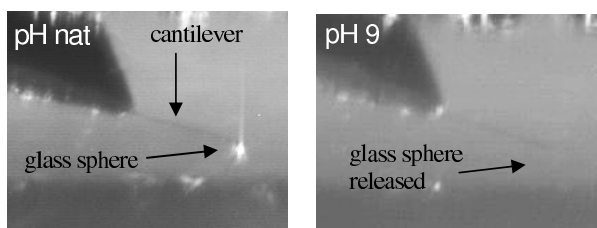
V. APPLICATION OF FUNCTIONALISED SURFACES IN MICROMANIPULATION

The behaviour described in table I shows a transition between attraction in natural pH and repulsion in pH 9. This switching behaviour can be used to control the grasping and the release of a micro-object manipulated with a microgripper. The figure 8 shows first experiments made with the AFM with a tipless cantilever (PointProbe Technology), functionalised with APTES. These experiments have been repeated six times on different spheres. Using attractive force (natural pH), a glass sphere whose diameter is around 50 micrometers is "grasped" with the cantilever (figure 8(a)). The increase of pH inverts the behaviour and at pH9, the sphere has been released (figure 8(b)).

VI. CONCLUSIONS AND FUTURE WORKS

A. Conclusions

In this paper, we have studied interaction behaviour between two functionalised surfaces and between functionalised and neutral surfaces. The experiments were done



(a) Grasping of the sphere with cantilever at natural pH (b) Release of the sphere at pH9

Fig. 8. Grasping and Release of the sphere with functionalised cantilever

in function of the pH of liquid and compared with dry medium. The substrate were functionalised by two chemical compounds using silanisation (grafted of silane molecules). We have shown that the functionalisation and the pH of the medium could highly change the adhesion properties. The micro-assembly could be facilitated by a judicious choice of the media and of the functionalisation of both grippers and micro-objects. We have shown that the pH can be used to control the release of a non-functionalised object during micromanipulations. Furthermore, the use of functionalised grippers and objects enables to simply cancel adhesion on micro-objects. As adhesion is the current highest disturbance in micromanipulation, functionalisation is a promising way to improve micro-object manipulation in the future.

B. Future Works

This paper consists in a proof of concept of a new promising micromanipulation method. The complete characterisation of this method based on repeatability measurements as well as reliability determination has to be performed. Future works will also focus on the implementation of this method which is able to cancel adhesion perturbations on two-fingered microgripper. Large blocking force required in microassembly will be thus possible.

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