

FUNCTIONALIZATION OF CARBON NANOTUBES BY ORGANOTITANATES IN AQUEOUS SOLUTION

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Abstract: The possibility of modification of carbon nanotubes with titanium stearate from aqueous solution was shown. The obtained modified CNTs are well soluble in toluene. For grafting of titanium stearate groups the surface of carbon nanotubes was pre-functionalized by oxidation. Modification of oxidized nanotubes with titanium stearate was performed from a solution containing dispersion of functionalized CNTs, triethanolamine stearate, and water-soluble complex of titanium with triethanolamine. This system is stable in solution at alkaline pH, and at low pH titanium stearate coagulates and joins to the CNT surface.

Introduction. For the distribution of carbon nanotubes (CNTs) in various polymer materials it is required to provide good wettability of the CNT surface with polymer. In the case of polar polymers it is most often achieved by oxidation of the CNTs surface with the formation of surface hydroxyl and carboxyl groups [1–4]. However, the introduction of CNTs into nonpolar media is a more complex task, which requires sophisticated methods of surface functionalization of CNTs or the use of non-traditional approaches [5–9]. Previously, we have shown the possibility of surface functionalization of CNTs with nonpolar groups by treatment of oxidized CNTs with solution of organotitanates in organic solvent [10]. The process of modifying CNTs surface proceeds due to reaction of carboxylic groups on the surface of CNTs with oligomeric organotitanates – the products of reaction of stearic acid with tetrabutyltitanate (TBT). Such modification cannot be carried out without pre-oxidation of CNTs. However, the disadvantage of this method is the need for a large amount of organic solvent such as toluene, per unit of carbon nanotubes mass. The problem could be solved through carrying out the process in aqueous solution. However, until now it could not be done because of insolubility of titanium stearate derivatives in water and hydrolytic instability of organic titanates containing reactive alkoxy groups.

The aim of this work is to study the possibility of functionalization of carbon nanotubes with titanium stearate by its deposition on pre-treated carbon nanotubes from aqueous solution.

Experimental. In the present work we have investigated the carbon nanotubes Taunit produced by NanoTechCenter Ltd. (Tambov). The CNTs Taunit have outer diameter of 20...70 nm and conical orientation of the carbon layers. For carrying out the process of functionalization carbon nanotubes with organotitanates it was needed initially to distribute CNTs in aqueous medium and this has been achieved by oxidative treatment of CNTs by the existing methods. The water-soluble form of CNTs Taunit was obtained by mechanical-chemical treatment of CNTs in the presence of sodium hypochlorite solution. Due to grafting of hydroxyl and carboxyl groups to the CNTs

surface the product obtained was infinitely soluble in water at simple mixing, even without addition of surfactant. At the CNTs concentration of 20 % and less the aqueous solution was liquid, at 25 – 35 % - gel-like, at 40 % and more – paste-like. The aqueous solution was stable at storage.

The starting compounds used were following: tetrabutyltitanate of “Technical” grade, triethanolamine and stearic acid - “Pure” grade, the carbon dioxide – “Technical” grade from gas-cylinder. Ultrasonic treatment was carried out with use of IL-10 unit. Distribution of particles by effective size in the diluted aqueous dispersion (about 0.1 g/l) was determined using the laser particle size analyzer NICOMP ZLS 380.

Photometric method was used to control the dispersibility of CNTs in toluene. Modified CNTs were dispersed ultrasonically in toluene, diluted with toluene to acceptable optical density and absorbance of the transparent gray solution obtained was measured at 500 nm with photoelectric colorimeter KFK-3.

Based on the optical density of the solutions of nanotubes and knowing their concentration in g/l, absorption coefficient was calculated in l/(g·cm). Previously, we have shown [10] that in these systems optical absorbance of solutions was proportional to the concentration of nanotubes, i.e., the Lambert-Beer law was obeyed, which makes it possible to calculate the absorption coefficient.

Results and discussion. The key to the successful modification of CNTs with organotitanates in aqueous medium is the choice of starting compounds, water-soluble and relatively stable for the duration of the process. It is known that the water-soluble inorganic titanium compounds are stable in acidic solution, but form precipitate of titanium hydroxide at neutral or slightly alkaline pH. On the other hand, the derivatives of stearic acid, when used as a hydrophobic component, are insoluble in acidic medium and can exist in solution, for instance as salts of stearic acid, only in alkaline medium. In addition, carbon nanotubes, functionalized with carboxyl groups, form stable colloidal dispersion in water only at neutral or slightly alkaline pH, while in acidic medium they coagulate. Thus, it turns out the incompatibility of all the three initial components. If you try to use the traditional method of deposition of metal stearates by mixing an acid solution of titanium salt with weakly alkaline solution of stearate, it is hardly possible to achieve a uniform coating of the CNT surface with titanium stearate because of the presence in the system of one liquid and two solid phases and effect of local supersaturation. Thus, the problem reduces to finding a suitable water-soluble reactants which are compatible in a matching range of pH.

It is known that dialkoxy-di-triethanolamine titanates obtained by partial transesterification of 1 mol of tetraalkoxytitanium derivatives with 2 moles of triethanolamine are hydrolytically unstable in aqueous solution [11]. Such is the commercially available bis-triethanolamine titanate. However, transesterification of tetraalkoxytitanium (TAT) with triethanolamine (TEA) and ethylene glycol ethers results in organic derivatives of titanium, fairly stable in aqueous solution [11]. Our experiments have shown that presence of ethylene glycol ethers is not obligatory to obtain a water-soluble titanium compound. It is sufficient to proceed the transesterification reaction in the TAT-TEA system until complete substitution of all butoxy groups in TAT with their distillation in form of n-butyl alcohol. Apparently, the relative hydrolytic stability of these compounds is associated with the formation of a chelate titanium complex with hydroxyl and amino groups of TEA. As an example, we give a description of synthesis method.

In a 1-liter round-bottom flask, totally immersed in the glycerin bath and fitted with a nozzle for distillation, was placed 200 g (0.5876 mol) tetrabutoxytitanium, 175.35 g TEA (1.1753 mol, 2 mol/mol TBT), and thoroughly mixed. Through the distillation adapter it was passed a thin Teflon tube that extended to the bottom of the flask, and current of argon (1 l/min) was passed through the tube during all process to prevent the reaction mixture from moisture of air. Temperature of the bath was raised to 120 °C and maintained for 2 hours in the range of 120...130 °C. First rapid distillation

of *n*-butanol formed occurred, at the end of the reaction time it ceased. Net weight of the product was 202.81 g, which is by 172.54 g less than the sum of masses of the initial reactants. The theoretical weight loss associated with removal of 4 moles of *n*-butanol per 1 mol of TBT should be 174.21 g. Thus, as the found mass loss is close to calculated, it can be assumed that almost all *n*-butoxy groups of TBT were replaced with triethanolamine groups. The product (hereinafter will be referred to as TEA-TBT) was a solid, a transparent mass, similar to rosin, at room temperature. At 80 °C, this mass softened into a viscous liquid. The substance was easily soluble in water and the aqueous solution was stable even after boiling. The aqueous solution of this substance had slightly alkaline pH due to the presence of amino groups of triethanolamine. The addition of mono-*n*-butyl ether of diethylene glycol (**MBDEG**) to this system also gave organotitanates stable in aqueous solution, in full compliance with the cited patent [11], but with the same result MBDEG can be used as a diluent for TEA-TBT synthesized as described above. The addition of MBDEG did not affected significantly by hydrolytic stability of TEA-TBT in aqueous solution.

Modification of carbon nanotubes was performed as follows. In 600 ml glass it was dissolved 2.00 g of TEA-TBT in 400 ml of water (which corresponds to 0.00584 mole titanate), and 6.00 g aqueous paste of water-soluble CNTs “Taunit” containing 43.8 % (2.628 g) of dry CNTs was added and stirred until dissolved. The solution was treated with ultrasound for 20 minutes at 50 % power at cooling in a water bath. The resulting black solution was transferred into 1-liter a round-bottomed flask with attachments for mechanical stirrer and gas supply. While stirring with mechanical stirrer (400 rpm) solution of triethanolamine stearate was added at room temperature. The latter was prepared by dissolving 3.323 g (0.01168 mol) of stearic acid and 2.388 g (0.01600 mol) of TEA in 200 ml of water with heating and stirring.

The mixed solution so obtained contained colloidal CNTs “Taunit”, TEA-TBT and triethanolamine stearate (2 mol of stearate per 1 mol of titanate). This solution was stirred for 30 minutes at room temperature, and then under continuing stirring (400 rpm) carbon dioxide (**CD**) was passed over the solution in the flask at a rate of 1 l/min. Due to dissolving CD pH of the mixture gradually lowered to neutral (6 by indicator paper). In about half an hour the system coagulated. Then feed of DC was reduced to 0.5 l/min and stirring continued for else one and half hour, after which the mixture left to stand until the next day. The precipitate was filtered off, thoroughly washed with water and dried in an oven for 4 hours at 100 °C.

The modified CNTs Taunit were obtained as gray pellets weighing 6.45 g, which is by 3.82 g more than the mass of initial CNTs. Theoretical increase of weight due to deposition of titanium stearate (in the first approach, counting it as the sum of titanium dioxide and stearic acid masses) is 3.88 g. Thus, with reasonable accuracy, we may assume that all the resulting titanium stearate was deposited on nanotubes.

Similarly, the synthesis of modified CNTs with other reagent ratio was performed. Conditions of synthesis and absorption coefficients (*K*) of toluene dispersion of modified CNTs are listed in the table. The values of *K* were calculated as $K = D/(Cl)$, where *D* – optical density of the dispersion; *C* – concentration of pure nanotubes (without modifier) in g/l; *l* – thickness of the cuvette (1 cm).

For comparison, the values of *K* for Taunit nanotubes dispersed in dimethylacetamide (**DMAA**) are presented. DMAA is one of the best solvents for dissolving the oxidized CNTs. Thus, the value of *K* for the solutions of CNTs in DMAA can be a point of comparison with other systems. St/Ti - the molar ratio of stearic acid:titanate; (St+TiO₂)/CNTs - weight ratio (stearic acid+titanium dioxide):CNTs.

The optical absorption coefficient, as was shown by our experiments, is sensitive to agglomeration of particles in solution. The smaller the value of *K*, the greater agglomeration. Thus, from the data presented in the table, it follows that for maximum dispersibility of modified CNTs in toluene optimal ratio of St/Ti = 2:1, at weight ratio

Conditions of synthesis of CNTs Taunit modified with titanium stearate and absorption coefficient K of their dispersions in toluene

Sample No	Conditions of synthesis		K (500-nm), l/(g·cm)
	St/Ti, mole	(St+TiO ₂)/CNT, mass	
1	3:1	2.13	27.6
2	2:1	2.21	26.8
3	2:1	1.48	32.6
4	2:1	1.14	28.8
5	2:1	0.74	19.2
6	1:1	0.83	6.9
7	Mechanochemically oxidized CNTs Taunit in DMAA		34.1
8	Not oxidized CNTs Taunit, processed in bead mill, in DMAA		24.2

(St TiO₂)/CNTs of about 1.5. Under these optimal conditions, the value of $K = 32.6$ for modified CNTs synthesized from aqueous solution, is only slightly less than the value of K for dispersion of mechanochemically oxidized CNTs Taunit in DMAA ($K = 34.1$). Reducing of St/Ti ratio to 1:1 leads to a sharp deterioration of dispersibility in toluene, probably due to decrease in the content of hydrophobic groups in the surface layer, while increasing of St/Ti ratio to 3:1, as well as variation in the weight ratio of (St TiO₂)/CNTs at constant St/Ti = 2:1, results in a slight decrease of K .

It was interesting to compare the values of K for toluene dispersion of CNTs Taunit modified which organotitanates in aqueous solution, as described above, and CNTs modified with oligomeric stearate-butoxy titanate (STBT) in toluene solution, similarly as we have done in [11]. To make this, we have conducted synthesis of STBT analogous to that described in [12]. Thus, 11.88 g (0.0350 mole) tetrabutoxytitanium, 98 ml of toluene and 19.86 g (0.0700 mole) of stearic acid was placed in a 250 ml round bottom flask equipped with adapter for distillation, through which thin Teflon gas-supplying tube was passed to the bottom of flask. While stirring in argon flow, the reaction mixture was heated (in glycerol bath) to 80 °C and stirred until dissolution of components. Then in argon flow at gradual increasing temperature to 130 °C distillation was conducted until condensate formed. The process took about 1 hour. The product which remained in flask was a viscous light-brownish liquid (25.81 g). This product, which according to [8] was a mixture of butyl stearate and STBT, was extracted three times with 40 ml of acetone to remove butyl stearate, and then rests of acetone were removed by heating substance at 55 °C in argon flow for one hour. It was obtained 19.15 g STBT, which was a waxy mass at room temperature.

For modification the mechanochemically oxidized CNTs Taunite (0.5 g) were sonicated in 50 ml of toluene solution of STBT (0.25...1 g). To measure the optical density the resulting solution was diluted with toluene. The absorption coefficients of the samples calculated on the mass of net Taunite were in the range of 30...32 l/(g·cm), which is close to the K values for samples obtained from aqueous solution at optimal ratio of components.

It was interesting also to compare the particle size distribution of CNTs Taunit modified with organotitanates in toluene and aqueous solution. In Fig. 1 – 4 there are shown particle size distributions for the dispersions of modified CNTs in toluene. Distributions are presented by the number of particles and the volume fraction of CNTs vs effective diameter.

Distribution for samples obtained by modifying CNTs Taunit in toluene at other amounts of STBT (0.25...1 g/0.5 g CNTs) are of the same type.

Thus, the samples of CNTs Taunit modified titanium stearate in aqueous solution well distributes in toluene and do not form large agglomerates. In general, effective average particle diameters for CNTs modified in water and toluene solutions are close.

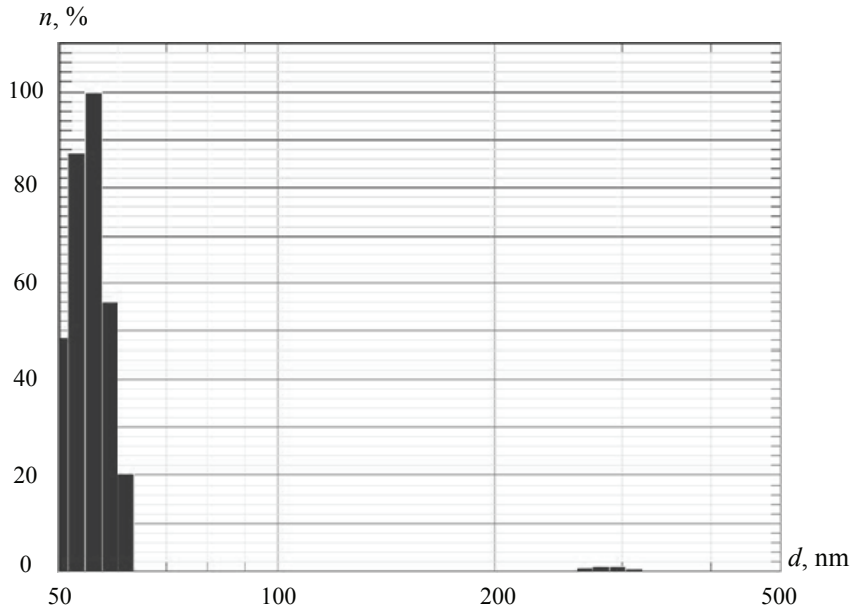


Fig. 1. Distribution of the number of particles on effective diameter of modified CNTs Taunit in toluene dispersion
(99.1 % of particles – 54.8 nm; 0.9 % of particles – 285.5 nm)

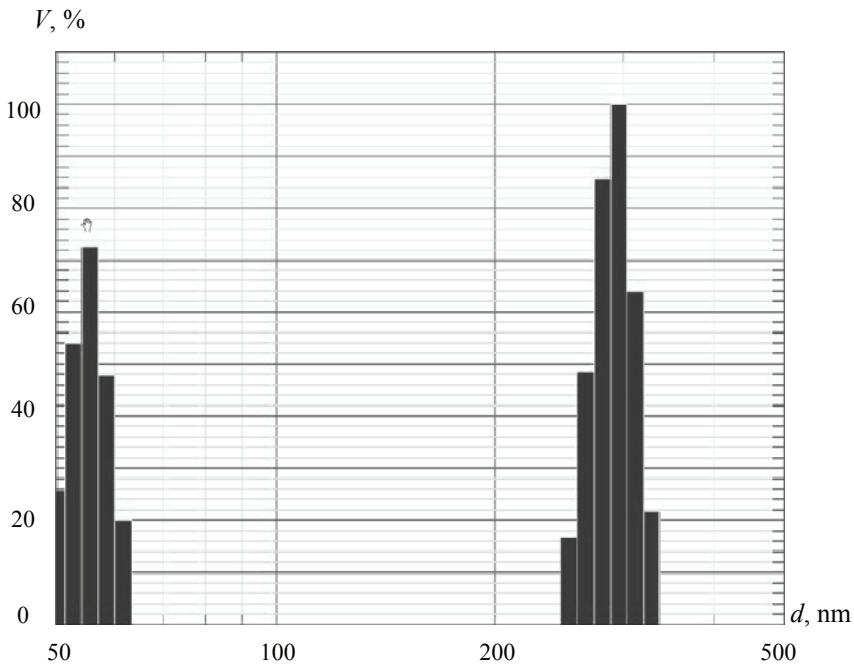


Fig. 2. Distribution of the volume fraction of particles on effective diameter of modified CNTs Taunit in toluene dispersion
(42.1 % of volume – 55.4 nm; 57.9 % of volume – 293.2 nm)

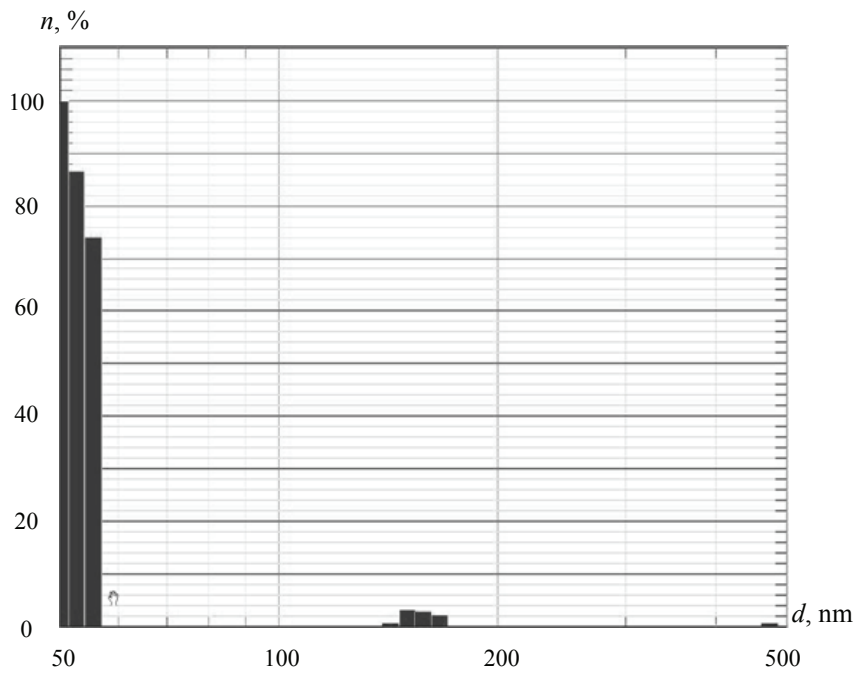


Fig. 3. Distribution of the number of particles on effective diameter of modified CNTs Taunit in toluene dispersion
(96.5 % of particles – 52.5 nm; 3.2 % of particles – 155.6 nm; 0.3 % of particles – 419.7 nm)

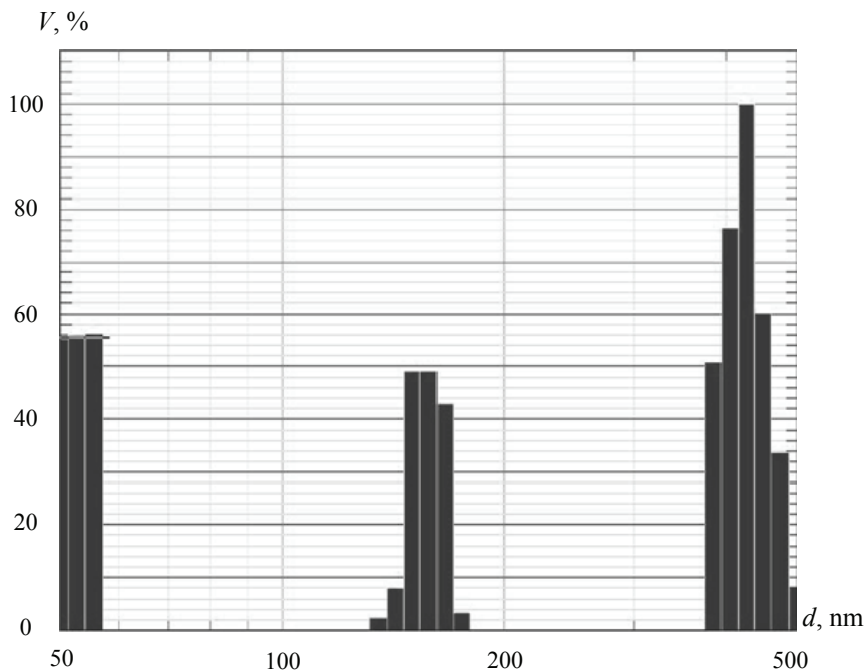


Fig. 4. Distribution of the volume fraction of particles on effective diameter of modified CNTs Taunit in toluene dispersion
(27.4 % of volume – 52.7 nm; 24.0 % of volume – 156.8 nm; 48.6 % of volume – 424.7 nm)

Conclusions. It is shown that carbon nanotubes can be modified with hydrophobic titanium stearate groups from aqueous solution. Optimal conditions for modifying are determined. The modified CNTs are well dispersible in toluene.

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Функционализация углеродных нанотрубок органотитанатами в водном растворе

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Ключевые слова и фразы: органические растворители; органические титанаты; углеродные нанотрубки; функционализация.

Аннотация: Показана возможность модифицирования углеродных нанотрубок (УНТ) стеаратом титана из водного раствора. Полученные модифицированные УНТ хорошо диспергируются в толуоле. Для прививки к углеродным на-

нотрубкам титан-стеаратных групп поверхность УНТ предварительно функционализировали путем окисления. Модифицирование окисленных УНТ стеаратом титана проводили из раствора, содержащего дисперсию функционализированных УНТ, стеарат триэтанолamina и водорастворимый комплекс титана с триэтанолamiном. Данная система устойчива в растворе при щелочном pH, а при понижении pH стеарат титана коагулирует и присоединяется к поверхности УНТ.

Funktionalisation der Kohlenstoffnanoröhre von den Organotitanaten in der Wasserlösung

Zusammenfassung: Es ist die Möglichkeit der Modifizierung der Kohlenstoffnanoröhre (KNR) von dem Stearat des Titans aus der Wasserlösung angeführt. Die erhaltenen abgeänderte KNR werden im Toluol gut dispergiert. Für das Okulieren zu den Kohlenstoffnanoröhren der titansthearatischen Gruppen wurde die Oberfläche von KNR mittels der Oxydierung vorläufig funktionalisiert. Die Modifizierung der oxidierten KNR vom Stearat des Titans wurde aus der Lösung, die die Dispersion der funktionalisierten KNR, das Stearat des Triethanolamines und den wasserauflösbaren Komplex des Titans mit dem Triethanolamin enthält, durchgeführt. Das vorliegende System ist in der Lösung bei alkalischen pH standfest, und bei der Senkung von pH koaguliert das Stearat des Titans und schließt sich an die Oberfläche von KNR an.

Fonctionnalisation des nanotubes carboniques par les organotitanates dans une solution aqueuse

Résumé: Est montrée la possibilité de la modification des nanotubes carboniques (NTC) par stéarate de titane de la solution aqueuse. Les NTC modifiés reçus se dispersent bien dans le toluène. Pour inoculer les groupes titane-stéarate des nanotubes carboniques la surface des NTC est préalablement fonctionnalisée par la voie de l'oxydation. La modification des NTC axydés par stéarate de titane a été effectuée à partir de la solution qui contenait la dispersion des NTC fonctionnalisés, le stéarate de triéthanolamine et le complexe soluble dans l'eau de titane avec triéthanolamine. Ce système est résitant dans la solution avec pH alcalin. Lors de la diminution de pH le stéarate de titane coagule et se rallie à la surface des NTC.

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