Soldering scrap, generated in large quantities by modern electronic industry, is basically lead-free but contains significant concentrations of copper and silver. This is a valuable raw material, and high purity tin can be obtained by electrolytic refining. There are a number of advantages in applying pure hydrochloric acid–tin chloride media, if the difficulties of solution stability, electrolytic efficiency and deposit morphology can be overcome. An aqueous procedure was developed on the basis of potentiodynamic studies and long-term electrorefining experiments. It can be used for an efficient purification of the valuable waste material in a single operational step. The formation of chloro-complex ionic species may offer a beneficial level of natural inhibition, therefore the inefficient and in some respects harmful organic additives should be omitted. The tendency of Sn(II) oxidation and precipitation can be overcome by properly controlling the concentration of the main components in the electrolyte solution. The virtual cathodic current efficiency can be increased close to the theoretical value by optimizing the composition of the electrolyte solution, the applied apparent current density and the technological parameters of the PCR (periodical current reversal) electric supply. The loose structure of a deposited metal may satisfy the technical requirements but it requires special cell arrangement and care during operation. Electrolyte circulation should only be applied for the control of composition. The attainable purity – of close to 99.99% – surpasses the standard technical requirements.

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There are different solutions which can be applied for tin refining. Alkaline baths are not favorable because of the required high temperatures (~80 °C) and stability of the tetravalent state, which implies twice as much electric charge as the divalent tin ions usually stabilized in acid media (Halsall, 1989; Kekesi et al., 2000). Their only advantage is the relatively compact deposit. Acid electrolyte solutions, on the other hand, generate more anode slime with about four times higher tin content and it is almost impossible to obtain a dense cathodic deposit (Wright, 1967). The conventional multi-component baths consist of SnSO4 (30–40 g/l tin), cresylic–phenyl sulfonic acid (40–100 g/l) and free sulfuric acid (40–80 g/l) with 1–2 g/l of β-naftol, or gelatine also added (Mackey, 1969; Bertha et al., 1979). The acid assures hydrolytic stability, improves conductivity and reduces the solubility of lead. Cresylic–phenyl sulfonic acid is extremely expensive, but it is necessary to improve solution stability through more soluble compounds of Sn(IV), whereas β-naftol, or gelatine promotes finer structures of the cathodic deposit.

In view of the shortcomings of the known tin electrorefining technologies and the possible savings on the material costs, it is worth examining the application of pure HCl–SnCl2 solutions. It also suits the production of pure tin, as any tin chloride entrapped in the cathode finally is removed by the final melting step to obtain a compact product. Addition of organic agents to the electrolyte solution may be omitted, as the Sn(II) ions form very stable chloro-complex ions, which may result in a favorable inhibition, controlling the fast electric charge transfer step and thus helping to avoid the growth of extremely rough crystals (Kekesi and Ishihki, 1997). The solubility of tin in chloride media is very high (Cotton and Wilkinson, 1967) and productivity is greatly increased by the applicability of higher current densities in chloride solutions. With the easily soluble anode made of the impure tin, cell voltage is low, thus electricity costs may be negligible. Nevertheless, the cathodic deposit is rough and dendritic, requiring special provisions for avoiding short circuits. A further precondition of applying the pure HCl–SnCl2 solution is to overcome the tendency of precipitation.

2. Dissolved species and precipitation

Dissolved tin forms chloro-complex ions in the HCl solution. The computer program ROCC developed at our department is useful in modeling the conditions. The distribution of tin among the various species in contact with metallic tin or air in solutions of varied chloride ion concentrations can be represented by the curves of Fig. 1A and B. The Sn(II) solution has a good stability in contact with metallic tin over the entire Cl~ ion concentration range, but it may be easily oxidized if the redox potential is increased by oxygen included from the air in the solution.

The reaction

\[
\text{SnCl}_x^{4-y} + \text{Sn} = 2\text{SnCl}_y^{2-x} + (y-2x)\text{Cl}^-
\]

ensures the stability of the Sn(II) form where the solution is in contact with metallic tin. This also implies some re-dissolution of the metal deposited at the cathode, thus it can reduce the current efficiency too. On the other hand, Sn(IV) ions can be formed by the oxidizing effect of air or the anode:

\[
\text{SnCl}_x^{2-x} + 0.5\text{O}_2 + 2\text{H}^+ + (y-x)\text{Cl}^- = \text{SnCl}_y^{4-y} + \text{H}_2\text{O}
\]

The standard potentials (Sn4+/Sn2+ = 0.154 V and Sn2+/Sn = −0.136 V) suggest that Sn2+ can be stabilized in aqueous solutions. However, the formation of chloro-complex ions modifies the distribution of tin between the two possible oxidation states. The required conditions for the anodic and the cathodic reactions can be outlined by the potential-pCl− diagram (Fig. 2A) constructed on the basis of the electrode potentials of the aquo-ions and the stability constants of the chloro-complex species. However, at lower Cl− and higher OH− ion concentrations, tin may form stable oxide or hydroxide compounds, resulting in the precipitation and the consequent loss of solution stability. The most unstable compound to be first precipitated is SnO2. At further increased pH, the precipitation of Sn(OH)4 and finally H2Sn(OH)6 can also take place (Kelsall and Gudyanga, 1990). The possibility of precipitation can be assessed by the relevant potential-pH diagram shown in Fig. 2b (Kelsall and Gudyanga, 1990). Below zero pH – corresponding to the 1–2 M HCl range – Sn(OH)4 is not formed, but SnO2 may arise if the electrode potential is higher than −0.15 V. Therefore formation of stannic oxide precipitation is likely at the area of the anode and the surface of the solution. Comparing Fig. 2A and B suggests that by controlled anode potential the chlorocomplex Sn(II) species can be formed and the formation of SnO2 can be avoided. The conditions allowing the generation of chloro-complex Sn(IV) species
and SnO₂ virtually coincide. Higher than ~0 pH values are unfavorable for the danger of excessive SnO₂ formation, however lower pH values are not desired because of the increased cathode corrosion, the danger of hydrogen evolution and economy of the operation. Thus 1 M HCl solutions have been in the focus of further attention.

As a result, the surface of the electrode polarized to the dissolution of tin can be quickly covered by tin-oxide and hydroxide compounds mixed with detached metal particles. Samples of this material were analyzed by X-ray diffractometry to determine the mineralogical composition. Fig. 3 shows that the Cu–Sn phase is predominant and copper can be found in elemental and also oxidized forms. SnO₂ appears to be a minor phase. As a result of uneven dissolution, tin particles are also incorporated.

In view of the solutions in contact with ambient air, either in operation or during pauses, the possible rate of Sn(II) oxidation under stationary conditions is of practical interest for devising the process. Oxidation with air is compared in Fig. 4A an b for the pure and the pyrogallol containing originally 10 g dm⁻³ Sn(II)–1 M HCl solutions. The concentrations of the Sn(IV) species generated can be indicated by the corresponding changes in the light absorption spectra, using a phenyl fluorone analytical reagent (Cotton and Wilkinson, 1967). The net light absorption value is calculated by subtracting the absorbance of the HCl–phenyl fluorone solution.

The oxidation of dissolved Sn(II) by air is slow. It can be even relatively suppressed by the addition of pyrogallol as an anti-oxidant. The changes in the absolute concentrations (Fig. 4B) were determined by the direct iodometry of Sn(II) and the analysis of the total tin concentration by the same method after a complete precipitation and re-dissolution of the tin content under nitrogen atmosphere in boiling 6 M HCl assisted with platinum catalyst. Pyrogallol is a well known organic antioxidant. Its closed phenol ring opens on reaction with dissolved oxygen and simple compounds, like acetic acid and carbon dioxide are formed:

\[ 2C_6H_6O_3 + 3O_2 \rightarrow 3CH_3COOH + 6CO_2. \] (3)

This may protect Sn(II) from oxidation to a certain extent. If the tin chloride solution is kept open to the air and also in contact with metallic tin, the total Sn concentration increases by the combined effect of reactions (Bertha et al., 1979 and Carlin, 1998). The rise in the total tin concentration depends on the rates of these two reactions, determined by the supply of oxygen if the active surface of the metallic tin is large. Although the oxidation by air is relatively slow, it may eventually cause instability of the solution. Solubility of SnCl₂ is approximately 80–90 g/dm³ in water at 0 °C (Muller and Seward, 2001), thus the increasing total tin concentration may result in SnCl₂ precipitation in highly concentrated solutions.

If Sn(IV) is also present, a white-yellow stannic acid type (SnO₂·nH₂O) precipitation may also arise (Muller and Seward, 2001). It can be observed in the solution standing in contact with air and metallic tin for several days. Fig. 5A shows the formation of a precipitate (of white color) consisting of fairly large crystals, and Fig. 5B gives the picture of the dispersed finely crystalline precipitate (of yellowish color). The corresponding X-ray diffractograms – marking the peaks of the SnCl₂ compound – are shown in Fig. 6A and B. The typical component in the rough precipitate formed with white color in the low oxygen solution is SnCl₂, whereas the fine precipitate formed under more oxidizing conditions is SnO₂·nH₂O.

![Fig. 2. Potential-pCl⁻ (A) and potential-pH (Kelsall and Gudyanga, 1990) (B) diagrams in the Sn–H₂O–Cl system.](image)

![Fig. 3. Compounds found at the surface of the anodically dissolved raw tin material.](image)
conditions consists also of Sn₆O₄(OH)₄, Sn [O₂] and H₂SnCl₆(H₂O)₁₀ besides a relatively lower but still dominant amount of SnCl₂.

According to Fig. 1B and Eq. (2), oxygen may oxidize Sn(II) ions to form [SnClₓ]₄⁻ chloro-complex species in solution, but at low acid concentrations precipitating hydroxides or oxides may arise:

\[
\begin{align*}
\text{Sn}²⁺ + \frac{1}{2} \text{O}_2 + 3\text{H}_2\text{O} & \rightarrow \text{Sn(OH)}₄ + 2\text{H}^⁺, \\
\text{Sn(OH)}₄ + \text{Sn(OH)}₂ & \rightarrow \text{Sn}_2\text{O}_5 \text{H}_₂\text{O} + 2\text{H}_2\text{O} \rightarrow 2\text{SnO}_₂ + 4\text{H}_₂\text{O}.
\end{align*}
\]

The oxidized compounds may interfere with the normal electrode processes and finally cause the decomposition of the solution. Therefore,

Fig. 4. The generation of Sn(IV) species by air oxidation in the originally 10 g dm⁻³ Sn(II)–1 M HCl 50 cm³ starting solution. (A, B — no additive, C — 1 cm³ 0.1 mol/dm³ pyrogallol added).

Fig. 5. The formation of different precipitates in the (originally 10 g/dm³ Sn (A) 1 M HCl) solution on long time standing in contact with metallic tin and air.

Fig. 6. Diffractograms of the white (A — SnCl₂, Sn₄(OH)₆Cl₂) and yellowish (B — SnCl₂, SnO₂(OH)₆, SnO₂, H₂SnCl₆(H₂O)₁₀) precipitates formed in the solution on long standing in contact with metallic tin and air.
the electrolytic refining of tin in HCl solutions requires counteracting the tendency of Sn(II) oxidation and the control of Sn concentration at the same time.

3. Experimental procedure

In order to decide the suitable conditions for the electorefining process, primarily the anodic and the cathodic reactions were studied by the potentiodynamic technique in solutions of different compositions. Determining the main characteristics of the process, such as current efficiency, deposit morphology and purity, however, required relatively long experimental runs with a laboratory scale electorefining cell.

The electrolyte solution was prepared by dissolving the required amount of reagent grade tin powder in boiling 6 M HCl in a heated reactor flask equipped with a reflux condenser, followed by dilution. Preliminary studies of the electrode processes were carried out by the potentiodynamic technique, applying the standard set-up with a saturated calomel electrode (SCE) reference, a Pt spiral counter electrode and a tin plate with 1 cm² prepared flat surface used as the working electrode. The voltage between the working and the reference electrode was controlled by an Electroflex EF 435C potentiostat. The generated current was recorded by the attached computer using an EF 2105 AD/DA converter interface. The measurements started from the zero current equilibrium potential with 10 mV steps and 5 s setting periods. The apparent current density refers to the fresh geometric surface area of the electrode.

The anodes used for the electorefining experiments were prepared by remelting and casting the lead free soldering scrap (obtained from JABIL-Hungary Electronics Co.). The amount of dross generated (10–20% of the raw material) was skimmed with aluminum tools before casting the melt into anode slabs. The copper starting cathode sheet was masked around the 9 cm² active surface, which was coated with a compact layer of tin deposited by pre-electrolysis. It was polished to yield approximately the same surface quality before every run. The experimental cell was made from a 1 cm thick polycarbonate plate. A fine polymer filter mesh was inserted between the anodic and cathodic compartments, as shown in Fig. 7A, to avoid slime dispersion and to prevent the roughly growing crystals from contacting the slimy anode surface. Most often during the process, long dendritic crystals were seen developing, as Fig. 7B and c shows, which were periodically pressed back gently by a Teflon spatula. Two regulated direct current supplies were used for the PCR experiments. They were periodically switched over by a computer controlled electronic circuit developed in our laboratory. The forward and reverse current intensities were equal and the usual forward and reverse period times were 4 and 0.2 s, respectively. Voltage and current data were recorded by a computer equipped with a National Instruments NI-USB 6212 AD/DA interface and a NI Labview 8.5 software for data acquisition and processing.

In order to determine the change in the cathodic current efficiency, the current was regularly stopped and the deposit was removed during the electrolysis and measured after washing and drying.

The gross current efficiency, expressing the utilization of the total electric charge, was expressed as:

$$H_{\text{gross}} = \frac{\Delta m_{\text{Sn}}}{t_f \int_{t_i}^{t_f} \left( \frac{I_+}{I_+ - I_-} \right) dt}$$

where $\Delta m_{\text{Sn}}$ is the mass increment of the cathode in the $(t_f - t_i)$ duration of electrolysis, $I_+$ and $I_-$ are the absolute forward and reverse currents in the $t_i$ and $t_f$ corresponding periods, $F$ is the Faraday constant $z$ is the valence of the electro-active ions and $A_{\text{Sn}}$ is the atomic mass. A value of the current efficiency was expressed assuming the deposition of the Sn(II) species. Although these species are predominant in the examined solutions, they cannot be exclusive, therefore this value is considered as a “virtual current efficiency”. Thus for example with $t_+/t_- = 20/1$ and $I_+ = I_-$ the maximum gross current efficiency cannot be higher than 91%, assuming the reduction of Sn(II) species at the cathode.

4. Experimental results and discussion

Results of the potentiodynamic preliminary experiments had shown that the anodic process allows high current densities even with stationary solutions. No passivation was observed as far as approximately 1 V above the equilibrium potential, which allowed extremely high (~0.7 A/cm²) apparent current densities. A fast rate of metal deposition and thus high cathodic currents are attainable already at 10 g/dm³ tin concentration, which may be a practical setting. The current attributed to hydrogen evolution at the surface of the tin working electrode was found negligible at all the examined cathodic potentials below 2 mol dm⁻³ HCl concentrations. The steep and steady rise of the apparent current density with the increased cathodic polarization is enhanced by the deposition of tin in a rough, dendritic form, increasing the effective cathode surface. This allows a steep rise of the cathodic current with increased overpotentials. The actual current densities are lower than the apparent values obtained from the original (geometric) surface. Fig. 8 shows the cathodic polarization curves obtained in stationary solutions of different tin and HCl concentrations.

The tin working electrode is immediately attacked by Sn(IV) species on immersion in the solution. Before the start of the cathodic reduction, the local concentration of Sn(II) around the tin plate is increased
through the spontaneous dissolution reaction (Bertha et al., 1979). Therefore the initial section of the polarization curve corresponds to a locally higher tin concentration. Tin concentration beyond 10 g/dm³ only slightly increases the attained cathodic current. Excessive tin concentrations may cause precipitate formation, and 10 g/dm³ is well enough for allowing high current densities to be reached. As low as 0.5 mol/dm³ HCl concentration causes instability, rendering part of the tin content inactive, therefore the corresponding curve is lower than the rest of the quite uniform curves at higher HCl concentrations. On the other hand, a slight hydrogen evolution could be observed at high acid levels. Therefore, 1 M can be considered as a good choice of HCl concentration for the refining process. The effect of solution agitation has also been tested. The stirring rates beyond ~200 r.p.m. did not cause further significant changes to the polarization curves. The sections at higher current densities (from ~1000 A/m²) are only slightly higher at stirring rates in the 200–600 r.p.m. range. These results suggest that the planned electrorefining process can be implemented in solutions agitated only by the forced circulation required for the stabilization of the solution parameters.

The main electrorefining experiments with 2 h runs could clearly show the characteristic current efficiencies and deposit structures. The PCR technique was used as a basic tool for improving the conditions, therefore the effect of the PCR cycle settings was first examined. As shown in Fig. 9A, low period time ratios can result in severe losses of current through the forced or spontaneous re-dissolution of the cathodic deposit. Relatively longer forward current periods, on the other hand, can increase the current efficiency to a certain limit. However, higher than 20 \(t_+ / t_-\) ratios are not efficient because the benefits of current reversal – by reducing the anode potential and refining the cathodic deposit structure – are becoming negligible. Fig. 9A also shows that increasing the apparent current density to ~1000 A/m² significantly increases the virtual gross current efficiency. Beyond this value hydrogen evolution may curb the current efficiency. Therefore, this is preferred as a practical setting in the proposed electrolyte solution. According to Fig. 9B, the long-term electrorefining experiments proved the reason for choosing the 10 g/dm³ Sn–1 M HCl solution composition, suggested by the preliminary potentiodynamic results. This combination offered the highest current efficiency. The virtual current efficiencies plotted in Fig. 9A and B refer to the freshly prepared \(\text{SnCl}_2–\text{HCl}\) solutions and 2 hour electrolysis time. Repeating the electrolysis run with the same solution gave 5–10% higher current efficiencies in all cases. It may indicate that the inadvertent initial
Sn(IV) concentration is reduced during the first electrorefining run, therefore the repeated experiment could be run under more favorable solution characteristics. Applying stronger circulations of the electrolyte solution is virtually ineffective in this aggressive electrolyte solution. Increasing the flow rate of forced circulation may improve conditions of mass transfer and tin deposition, but it also enhances chemical re-dissolution, especially in the fresh solutions. The only benefit of the stronger forced circulation is in the promotion of a shorter outgrowing crystal structure. The effect of temperature is weak, because it promotes both the useful processes of cathodic deposition but also the chemical re-dissolution. Forced circulation should only be used to maintain the electrolyte conditions at the convenient temperature set by the natural heat balance of the cell.

The morphology of cathodic deposition is basically roughly dendritic. Fig. 10A shows the typical structures obtained during the prolonged 8 h experimental electrolysis runs applying the conditions optimized according to the results in Figs. 8 and 9. Even longer experiments have also been conducted, leading to consistent results. The effect of adding an organic inhibitor for producing finer structures was tested by repeating the 8 h experiment with 0.267 g/dm$^3$ gelatine in the solution. The most obvious effect of gelatine addition was the observed hydrogen evolution and porous deposition in the initial stages of the electrolysis. The deposit structure was finer, but the grains were porous, almost pulpy. According to the typical structures shown in Fig. 10B, a compact deposit could not be obtained in this way, and neither by varying the concentration nor the type of the inhibitor additive. Although the structure of the deposit is typically loose, it can be controlled by mechanical compacting and applying a filter mesh separation between the anode and cathode compartments. The product is, however, easily removed from the mother plate. It can be easily melted directly after washing, or even better by immersion in a molten tin bath.

Changes in the compositions of the solutions in the anode and cathode compartments were examined by analyzing samples taken periodically during the 8 h electrolysis runs. For representing the average composition of the solution in the compartment, a gentle stirring was also applied after the cathode was removed for measuring the mass of the deposit produced in the corresponding time interval. Based on the periodically measured weights of the removed deposit batches, the change of the current efficiency was also detected. In the case of the additive free pure solution, the virtual gross current efficiency increased from 85 to 87% during the 8 h run. In the case of gelatine addition, it increased from 78% to 82%. It also indicates that the organic additive may considerably decrease the current efficiency, although the morphology of the deposit is virtually not improved. The adverse effects of the additive were obvious especially at the first 4 h of the electrolysis. The total tin concentration was continually increasing in both compartments of the cell, while the Sn(IV) concentration remained low as shown in Fig. 11. The main cause of the observed increase in the tin concentration must be the corrosion mechanism by Eqs. (1) and (2). As anodic oxidation to Sn(IV) does not lead to
increasing total tin concentration, some of the primarily dissolved Sn(II) species should be oxidized by ambient air and the resulting Sn(IV) may re-dissolve the corresponding amount of the deposited metal. Thus the Sn(IV) concentration can stay stable and the total tin concentration increases continually. The increase in the tin content of the pure solution was 0.61 g during the 8 h electrolysis, but the measured overall current efficiency shows 0.66 g deficit from the theoretically expected mass. The difference (0.05 g) may be attributed to the relatively negligible hydrogen evolution at the cathode. As the acid concentration is virtually stable or slightly increasing, any possible hydrogen evolution at the cathode must be counterbalanced or even surpassed by oxygen evolution at the anode. However, in the case of gelatine addition, the missing tin mass calculated from the current efficiency is 1.4 g, whereas the increase in the tin content of the solution was only 0.85 g. In this case the difference is 0.55 g, which indicates a relatively greater rate of hydrogen evolution. This can be attributed to the effect of the added gelatine inhibiting the cathodic deposition of tin. Therefore the addition of gelatine, as an organic inhibitor, has definitely harmful effects on the efficiency of the process. Another negative effect of organic inhibitors may be the deterioration of cathode purity. It is important if a special grade tin is the aim.

The cathodic deposit has a higher purity than required for ordinary technical purposes. A good indication of the purification efficiency is given by the comparison of the compositions of samples taken from the raw anode material and the deposit produced at the cathode. Analysis of the samples was carried out by ICP OES (inductively coupled plasma optical emission spectrometry) after complete dissolution in boiling 6 M HCl. Table 1 shows the impurity concentrations in the tin crystals obtained after 4 and 8 h of electrolysis. The raw anode material and the deposit produced at the cathode. Analytical investigations have shown that 1 M HCl and 10 g/dm³ Sn may be the optimum composition of the solutions. High current efficiencies, approaching the theoretical value could be reached with apparent current densities of approximately 1000 A/m², applying the PCR technology with 20:1 time ratio of forward to reverse current periods. Experiments have proved that solution agitation and organic additives may not improve the main characteristics of the process. The structure of the cathodic deposit is typically loose and the crystals are dendritic. This feature cannot be much improved. However, it is easily removed and our experience has shown that melting by submersion in an existing tin bath, or simply by rapid heating starting from the wet state, after washing, generates virtually no dross. The produced tin is of ~99.9% purity. The favorable performance of the HCl-based electrolyte solution has proved the expected beneficial effects of complex formation, high solubility and rapid mass transfer. The recovered pure tin and the possible extraction of extra values from the anode sludge warrants implementation of the flexible process. Assuming a clean handling of the cathodic product, a special grade material, suitable for advanced applications in the electronic or food industry is obtained.

Table 1

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5. Conclusions

Recycling of soldering scrap collected from the electronic industry carries great economical potential. Elimination of the impurities dissolved by the lead-free tin soldering bath requires chemical metallurgical processing. The possibility of a novel aqueous technology based on the application of pure HCl solutions was proved by the experimental results. Potentiodynamic and long-term electrorefining investigations have shown that 1 M HCl and 10 g/dm³ Sn may be the optimum composition of the solutions. High current efficiencies, approaching the theoretical value could be reached with apparent current densities of approximately 1000 A/m², applying the PCR technology with 20:1 time ratio of forward to reverse current periods. Experiments have proved that solution agitation and organic additives may not improve the main characteristics of the process. The structure of the cathodic deposit is typically loose and the crystals are dendritic. This feature cannot be much improved. However, it is easily removed and our experience has shown that melting by submersion in an existing tin bath, or simply by rapid heating starting from the wet state, after washing, generates virtually no dross. The produced tin is of ~99.99% purity. The favorable performance of the HCl-based electrolyte solution has proved the expected beneficial effects of complex formation, high solubility and rapid mass transfer. The recovered pure tin and the possible extraction of extra values from the anode sludge warrants implementation of the flexible process. Assuming a clean handling of the cathodic product, a special grade material, suitable for advanced applications in the electronic or food industry is obtained.
Acknowledgments

Work on the subject started under the auspices of the REG_EM_KFI_09 (2009) project, funded by the Hungarian Office for Research and Development, NKTH. This research was supported by the program TÁMOP 4.2.1.B-10/2/KONV-2010-0001.

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