PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF THE SOLID COMPONENT OF WELDING AEROSOL

INTRODUCTION

Atmospheric emission of welding aerosols is a result of complex physical and chemical processes taking place in the course of welding. The solid component of welding aerosol (SCWA) is the air-dispersed particulate formed out of the welding arc in consequence of the oxidation and condensation of vapors of components of electrode coatings, welding fluxes, and metals. A composition of the gaseous component of welding aerosol (GCWA) depends on the nature of materials applied and welding conditions influencing the proceeding of reactions following by HF, SiF₄, CO, NOₓ, and O₃ formation [1–5]. Among the listed gases, ozone is an extremely hazardous compound with maximum permissible concentration (MPC) within working areas of only 0.1 mg/m³. Taking into account the extent of welding and related fabrications as well as the variety of welding techniques and materials, the actual problem is not only to decrease hazardous effect of SCWAs and GCWAs on the environment and operating personnel but also to recycle solid wastes for obtaining products of industrial and domestic use.

A possibility of SCWA application as sorbents for retaining acid gases and petroleum products, charges for polymer composites, and catalysts for high-temperature (700–900 °C) oxidizing condensation of methane was first demonstrated in [4, 6]. There was clear evidence that catalytic performance of SCWAs in chemical reactions of any type depended on their chemical and phase composition. Chemical and phase composition of SCWAs is a consequence of the nature of both weld materials and welding electrodes, of electrode coating materials and welding conditions [7–17]. As far as we know, there are no data in literature concerning a phase composition of SCWA formed as a result of metal welding by a TsL-11 type electrode (ISO E19.9NbB20). Systematic studies concerning the use of solid wastes for obtaining catalysts for ozone decomposition are also absent there. The only known case is the application of a sludge underflow formed in the process of water purification and enclosing iron oxides for obtaining cement containing catalysts for ozone decomposition at its concentration of ca. 2·10⁴ mg/m³ [18].

The aim of the work was to identify a phase composition of the solid component of welding aerosol produced as a result of welding by the TsL-11 type electrode (SCWA-TsL-11) and to study catalytic performance of the latter in the reaction of ozone decomposition at ozone initial concentrations ranging from 1 to 100 mg/m³.

EXPERIMENTAL

The welding fume fractions of the SCWAs with the aerodynamic diameter ≤ 1 μm formed in the process of metal arc welding by the 3 mm diameter TsL-11 type electrodes (ISO E19.9NbB20) with the carbonate-fluorite electrode coating were selected for the study. Welding was performed under conditions of direct current, reverse polarity, U = 33 V, I = 140–150 A, and the welding speed, V, of 4.5 mm/s. TsL-11 type electrodes produced
from steel wire of Sv-08Kh19N10B grade consisting of Fe (67.0 wt. %), C (0.05–0.10 wt. %), Mn (1.2–1.7 wt. %); Si (0.7 wt. %), Cr (18.5–20.0 wt. %), and Ni (9.0–10.5 wt. %), and having a carbonate-fluorite coating consisting of ferromanganese (5.0 wt. %), marble (54.0 wt. %), derbyshire spar (15.0 wt. %), quartz (9.0 wt. %), ferrosilicon (5.0 wt. %), and ferrotitanium (15.0 wt. %) were used in manual arc welding of high-alloy steels, high alloys, and corrosion-resistant chromium-nickel steels [11].

SCWA-TsL-11 samples were characterized by X-ray diffraction phase analysis, IR spectroscopy, and pH-metry. In addition, they were tested in the reaction of low-temperature ozone decomposition.

The samples were identified based on X-ray diffraction phase analysis data recorded on a Siemens D500 diffractometer (CuKα radiation, λ = 1.54178 Å) with a secondary beam graphite monochromator. The phases were identified with the help of ICDD (International Centre for Diffraction Data) PDF-1 databases provided as a part of the Siemens D500 diffractometer software.

Infrared analysis was carried out using a Perkin Elmer FT-IR Spectrometer with resolution of 4 cm⁻¹; pellets consisting of 1 mg of the material under study and 200 mg of KBr were compressed under pressure of 7 tons/cm² for 30 s.

The equilibrium pH values measured in an aqueous suspension consisting of SCWA-TsL-11 (0.2 g) and distilled water (20 mL) were used to characterize protolytic properties of surface functional groups of the SCWA. The measuring was carried out by a pH-340 instrument with an ESL 43-07 glass electrode and an EVL 1M3 silver-chlorine electrode at continuous stirring of the suspension at 20 °C.

The catalyst samples (0.5 g) were tested using a gas-flow setup with a fixed bed reactor at 20 °C, relative humidity of 65 %, and the linear velocity (U) of an ozone-air mixture (OAM) equal to 3.2 cm/s. The ozone decomposition was monitored by measuring the final ozone concentration (Cf). The reaction rate (W) calculations based on the data of ozone concentration changing after OAM passing through the static bed of the catalyst were made using the following equation:

\[
W = \frac{w(C_{in} - C_{ff})}{m}, \text{ mol/(g·s)},
\]

where w = 1.67×10⁻² is the OAM volume flow rate, L/s; C_{in} and C_{ff} are the initial and final ozone concentrations in the OAM, mol/L; m is the mass of a catalyst sample, g.

The reaction rate values measured after one minute of OAM passing named as the initial reaction rate, W_{in}, were used to characterize the process.

The reaction rate constant, k_{1/2}, was quantified for the half reaction time, τ_{1/2}, i.e. for the moment of time when the degree of ozone decomposition became equal to 50 %, as follows:

\[
k_{1/2} = \frac{0.69}{\tau_{1/2}}, \text{ s}^{-1}.
\]

The amount of ozone entered into the reaction up to a moment of experiment termination (Q_{exp} moles of O₃) was calculated as a square of the corresponding ozonogram plotted as a ΔC_{O₃} vs. τ function.

To characterize protective behavior of the SCWA-TsL-11 samples, a period of time required for attaining of C_{o} = MPC_{O₃}, τ_{MPC}, was used.

RESULTS AND DISCUSSION

An X-ray diffraction pattern of the SCWA-TsL-11 sample (Fig. 1) demonstrates a high crystallinity of its individual phases. The most intensive reflections are observed in the range from 28 to 65 °.

The data concerning the phase composition of the SCWA-TsL-11 sample, some characteristics of its X-ray spectrum, i.e. angles of reflection, 2θ, the interplanar spacing (d, Å), both experimental and reference, and also the normalized reflection intensity, I_{0}, are presented in Table 1. By their help, a probability of formation of various intermetallics, oxides and fluorides of metals, silicate forms, etc. can be determined. Taking into consideration the chemical composition of both electrode wire and electrode coating, probable
phases are identified by the help of ICDD PDF-1 File, a part of the diffractometer software. Therefore reflections characterized by $I_N > 20$ are essentially considered, however, sometimes, peaks with $I_N < 20$ must be taken into account when their experimental and reference parameters are in close agreement.

![Graph](Image)

**Fig. 1.** The X-ray diffraction pattern of the SCWA-TsL-11 sample

Thirteen well-identified phases, such as manganochromite, (Mn,Fe)(Cr,V)$_2$O$_4$ (ICPDS 31-0630); magnesium silicate, MgSiO$_3$ (ICPDS 11-0273); α-quartz, α-SiO$_2$ [19]; goethite (red iron ore), Fe$_2$O$_3$ [19]; agacansite, β-Fe$_2$O$_3$·H$_2$O [19]; nickel fluoride, NiF$_2$ [19]; derbyshire spar, CaF$_2$ (ICPDS 35-0816); manganese oxide, Mn$_3$O$_4$ (ICPDS 13-0162); silicate of calcium and magnesium (mervinite), Ca$_3$Mg(SiO$_4$)$_2$ (ICPDS 35-0591); chromium oxide, Cr$_2$O$_3$[19]; nickel oxide NiO [19]; rutile, TiO$_2$[19]; and potassium chromate, K$_2$CrO$_4$[12, 19].

Because of superposition of many reflections, the phase identification requires to determine not only the sequence of reflections but also the presence of individual reflections of every phase in the X-ray spectrum. For instance, the most intensive reflection at $2\theta = 28.251^\circ$ ($d = 3.156$ Å) is a result of superposition of a CaF$_2$ peak and a MgSiO$_3$ peak with relative intensities according to reference data of 92 and 100 %, respectively. However, these phases have their second individual reflections at $2\theta = 46.999^\circ$ ($d = 1.931$ Å) for CaF$_2$ and at $2\theta = 30.804^\circ$ ($d = 2900$ Å) for MgSiO$_3$. Individual phase parameters also enable the identification of manganochromite having a vanadium impurity (ICPDS 31-0630) in its composition. Though the presence of ferrotitanium in the electrode coating and the fact that the relative intensity of the TiO$_2$ individual reflection has been found as 100 % [19], it is impossible to draw an unequivocal conclusion about the presence of TiO$_2$ in the SCWA-TsL-11 because of the absence of any individual TiO$_2$ reflection in its X-ray spectrum. The low-level ($I_N = 15$) reflection observed at $2\theta = 54.467^\circ$ ($d = 1.683$ Å) can be assigned to Cr$_2$O$_3$ (1.67 Å), Fe$_2$O$_3$ (1.69 Å), and TiO$_2$ (1.69 Å) or to the superposition of these individual peaks. It should be noted that Tanninen et al. [15] also did not reveal TiO$_2$ in the SCWA they investigated.

Due to the high contents of chromium and nickel in the TsL-11 electrode, Cr$_2$O$_3$ and NiO phases are clearly defined in the X-ray spectrum of its SCWA. Besides, chromium as K$_2$CrO$_4$ phase can be identified by its high-level ($I_N = 455$) individual reflection at $2\theta = 38.802^\circ$ ($d = 2.319$ Å). The presence of the sodium (potassium) chromate phase in the SCWA for an E314L type electrode was stated by Tandon et al. [12]. Iron oxides are present as goethite, Fe$_2$O$_3$, and agacansite, β-Fe$_2$O$_3$·H$_2$O, whereas no magnetite, Fe$_3$O$_4$, is identified. The low intensity of Mn$_3$O$_4$ reflection is an evidence of a negligible content of this phase in the SCWA-TsL-11 sample. Based on the most intensive peaks, crystallite sizes for some individual phases can be evaluated by the use of the Scherer equation. They are as follows: 89 nm for (Mn,Fe)(Cr,V)$_2$O$_4$, 83 nm for K$_2$CrO$_4$, 67 nm for CaF$_2$, and 65 nm for MgSiO$_3$. Other intensive reflections are superpositions caused by two or more phases. For example, an intensive reflection ($I_N = 658$) at $2\theta = 35.095^\circ$ ($d = 2.555$ Å) can be a superposition of peaks assigned to four phases: manganochromite, NiF$_2$, β-Fe$_2$O$_3$·H$_2$O, and MgSiO$_3$.

**IR spectral characteristics.** In the region from 4000 to 400 cm$^{-1}$, the SCWA-TsL-11 sample demonstrates absorption bands corresponding to stretching (3436 cm$^{-1}$) and bending (1637 cm$^{-1}$) vibrations of water molecules as well as stretching vibrations (1742 and 1381 cm$^{-1}$) of carbonate-carboxylate groups. The presence of the latter is due to the high-temperature oxidation of carbon monoxide formed as a result of the welding. The spectrum region from 1050 to 410 cm$^{-1}$ presented in Fig. 2 a characterizes stretching and bending vibrations of M–O (M = Cr, Fe) and Fe–OH bonds. For instance, absorption bands at 945 and 886 cm$^{-1}$ can be assigned to stretching vibrations of Cr–O in chromium oxide [20] although a band at 886 can be attributed also to a stretching vibration of Cr–O in a chromate ion (ν = 880 cm$^{-1}$) [12]. Potassium chromate was revealed by us in a solution obtained after hydrothermal treatment of a SCWA-TsL-11
sample at 60°C for 2 h. An intensive band at 597 cm\(^{-1}\) with shoulders at 615, 559, and 539 cm\(^{-1}\) is characteristic of Fe–O bond vibrations in oxides. It should be noted that exactly this band undergoes a change after the ozonization of a SCWA-TsL-11 sample (Fig. 2b).

Table 1. The results of X-ray phase analysis of the SCWA-TsL-11 sample

<table>
<thead>
<tr>
<th>Phase</th>
<th>2θ, dgs</th>
<th>I_N</th>
<th>d, Å</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>experimental</td>
<td>reference</td>
</tr>
<tr>
<td>(Mn,Fe)(Cr,V)(_2)O(_4)</td>
<td>18.072</td>
<td>122</td>
<td>4.905</td>
<td>4.89</td>
</tr>
<tr>
<td>Mn(_2)O(_4)</td>
<td>36.685</td>
<td>50</td>
<td>2.448</td>
<td>2.44</td>
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<tr>
<td>Mn(_3)O(_4)</td>
<td>56.060</td>
<td>344</td>
<td>1.639</td>
<td>1.63</td>
</tr>
<tr>
<td>β-Fe(_2)O(_3)(_2)H(_2)O</td>
<td>26.587</td>
<td>42</td>
<td>3.350</td>
<td>3.30</td>
</tr>
<tr>
<td>Mn(_3)O(_4)</td>
<td>39.290</td>
<td>15</td>
<td>2.291</td>
<td>2.29</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>46.383</td>
<td>37</td>
<td>1.956</td>
<td>1.96</td>
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<tr>
<td>NiO</td>
<td>73.876</td>
<td>21</td>
<td>1.282</td>
<td>1.28</td>
</tr>
<tr>
<td>NiO</td>
<td>78.794</td>
<td>11</td>
<td>1.214</td>
<td>1.21</td>
</tr>
<tr>
<td>NiO</td>
<td>89.748</td>
<td>11</td>
<td>1.092</td>
<td>1.09</td>
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<tr>
<td>NiO</td>
<td>109.011</td>
<td>28</td>
<td>0.946</td>
<td>0.946</td>
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<tr>
<td>NiF(_2)</td>
<td>63.909</td>
<td>24</td>
<td>2.433</td>
<td>2.40</td>
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<tr>
<td>CaF(_2)</td>
<td>43.298</td>
<td>27</td>
<td>2.088</td>
<td>2.08</td>
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<td>CaF(_2)</td>
<td>46.999</td>
<td>871</td>
<td>1.932</td>
<td>1.93</td>
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<tr>
<td>CaF(_2)</td>
<td>68.647</td>
<td>76</td>
<td>1.365</td>
<td>1.36</td>
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<td>CaF(_2)</td>
<td>87.378</td>
<td>113</td>
<td>1.115</td>
<td>1.11</td>
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<tr>
<td>MgSiO(_3)</td>
<td>27.079</td>
<td>21</td>
<td>3.290</td>
<td>3.30</td>
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<td>MgSiO(_3)</td>
<td>60.973</td>
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<td>1.518</td>
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<td>MgSiO(_3)</td>
<td>27.385</td>
<td>21</td>
<td>3.254</td>
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<td>MgSiO(_3)</td>
<td>30.804</td>
<td>50</td>
<td>2.900</td>
<td>2.90</td>
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<tr>
<td>MgSiO(_3)</td>
<td>38.802</td>
<td>455</td>
<td>2.319</td>
<td>2.32</td>
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<tr>
<td>MgSiO(_3)</td>
<td>42.631</td>
<td>147</td>
<td>2.119</td>
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<tr>
<td>MgSiO(_3)</td>
<td>55.796</td>
<td>325</td>
<td>1.642</td>
<td>1.64</td>
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<tr>
<td>MgSiO(_3)</td>
<td>56.473</td>
<td>178</td>
<td>1.628</td>
<td>1.62</td>
</tr>
<tr>
<td>MgSiO(_3)</td>
<td>62.639</td>
<td>61</td>
<td>1.482</td>
<td>1.48</td>
</tr>
</tbody>
</table>

Only one band at 605 cm\(^{-1}\) remaining in the spectrum after the ozonization can signify, as it was stated for chromium oxide [20], a change in the coordination number of iron in its oxides.

**Protolytic properties.** After contacting a SCWA-TsL-11 sample with water for 20 min, pH of this aqueous suspension decreases from 8.85 to 8.55 and does not change after that. A negative value of ΔpH (−0.3) indicates that the heterolytic dissociation of water molecules on Lewis acid sites of the solid surface proceeds in accordance with a basic mechanism E⁺…OH/H⁺.

**Catalytic properties.** The time dependence of the final ozone concentration obtained for ozone decomposition by SCWA-TsL-11 samples at ozone initial concentrations in the OAM varied from 1 to 100 mg/m\(^3\) is presented in Fig. 3.
It is clear that the profiles of kinetic curves depend on $C_{O_3}^{in}$ values. For example, $C_{O_3}^{f}$ is less than 0.1 mg/m$^3$ (MPC $C_{O_3}^{n}$) for 140 min at $C_{O_3}^{in}$ = 1 mg/m$^3$ (curve 1). This subcurve characterizes protective abilities of the SCWA-TsL-11 sample. After that $C_{O_3}^{f}$ slowly increases and attains its stationary level of 0.67 mg/m$^3$ in 1200 min whereas the ozone concentration at the reactor outlet increases rapidly up to its initial values at $C_{O_3}^{in}$ of 50 and 100 mg/m$^3$ (curves 3 and 4).

Table 2 summarizes some kinetic and stoichiometric parameters of the reaction.

<table>
<thead>
<tr>
<th>$C_{O_3}^{in}$, mg/m$^3$</th>
<th>$W_{in} \cdot 10^8$, mol/(g$\cdot$s)</th>
<th>$k_1 \cdot 10^3$, s$^{-1}$</th>
<th>$\tau_{1/2}$, s</th>
<th>$k_{1/2} \cdot 10^4$, s$^{-1}$</th>
<th>$Q_{exp} \cdot 10^6$, moles of $O_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.07</td>
<td>-</td>
<td>36000</td>
<td>0.2</td>
<td>1.86</td>
</tr>
<tr>
<td>10</td>
<td>0.63</td>
<td>3.6</td>
<td>3600</td>
<td>1.9</td>
<td>1.44</td>
</tr>
<tr>
<td>50</td>
<td>3.36</td>
<td>3.8</td>
<td>300</td>
<td>23.0</td>
<td>1.12</td>
</tr>
<tr>
<td>100</td>
<td>5.46</td>
<td>3.9</td>
<td>282</td>
<td>24.0</td>
<td>0.91</td>
</tr>
</tbody>
</table>

It can be seen that the initial reaction rate, $W_{in}$, increases in proportion to $C_{O_3}^{in}$ and the first-order reaction rate constant is changeless except for $C_{O_3}^{in}$ = 1 mg/m$^3$ when $C_{O_3}^{f}$ = 0. The latter makes impossible the calculation of the reaction rate constant. Other factors characterizing the kinetics of ozone decomposition are the half-reaction time, $\tau_{1/2}$, and the reaction rate constant corresponding to $\tau_{1/2}$, $k_{1/2}$. It is clear that the increase in $C_{O_3}^{in}$ results in a decrease in $\tau_{1/2}$ and in an increase in $k_{1/2}$. Such a variability of $k_{1/2}$ values and a decrease in the amounts of ozone entered the reaction, $Q_{exp}$, over periods of time equal to $\tau_{1/2}$ are evidence of a chain-radical reaction mechanism.

Taking into account the chemical and phase compositions of SCWA-TsL-11 and according to what is known about ozone decomposition reactions over both oxide catalysts [21] and atmospheric mineral aerosols [22], it can be concluded that the detected phases of manganochromite as well as oxides of iron, chromium, nickel, and manganese are the most probable catalysts of ozone decomposition. Among them, the highest catalytic activity in respect to the reaction under study is characteristic of manganese, nickel, and iron oxides [21]. Contribution of other phases, such as fluorides of calcium and nickel and silicates of magnesium and calcium, to the reaction most likely is minimal. In the case of SCWA-TsL-11, the catalytic performance of the listed active phases is limited.
individual oxides can be strengthened by a spinel, (Mn,Fe)(Cr,V)₂O₄, which is found not only as an individual phase but also as a combination with manganese and iron oxides (Table 1).

The IR spectrum of the SCWA-TsL-11 sample after its ozonization (Fig. 2 b) undergoes a notable change in the range of stretching vibrations of Fe–O bond whereas the bands assigned to vibrations of Cr–O bond in both Cr₂O₃ and chromate and Fe–O and Fe–OH bonds in iron oxides and spinels have been identified. Only one band assigned to vibrations of Fe–O bond after its position and form after the ozonization of the SCWA-TsL-11 sample.

The first reaction order with respect to ozone has been found at the initial step of the reaction of ozone decomposition over the SCWA-TsL-11 samples at the initial ozone concentration in the OAM ranging from 1 to 100 mg/m³. A deviation from the first reaction order in the case of half-reaction time is evidence of a chain-radical reaction mechanism. This agrees with the well-known conception of the ozone decomposition over individual metal oxides. The SCWA-TsL-11 sample provides air purification from ozone to the level less than MPCₖ₃ (0.1 mg/m³) at the initial ozone concentration of 1 mg/m³ (10 MPCₖ₃) for 140 min.

CONCLUSIONS

It has been found that the solid component of welding aerosol formed as a result of high-alloy steel welding by the TsL-11 type electrode (ISO E19.9NbB20) is a crystalline substance containing not less than thirteen phases. Crystallite sizes of individual phases are ranged from 65 to 89 nm. Manganochromite as well as oxides of iron, manganese, and nickel can decompose ozone at ambient temperatures.

The polyphase composition of the SCWA-TsL-11 has been confirmed by the results of IR spectroscopy. Stretching vibrations of both Cr–O bonds in Cr₂O₃ and chromate and Fe–O and Fe–OH bonds in iron oxides and spinels have been identified. Only one band assigned to vibrations of Fe–O bond after its position and form after the ozonization of the SCWA-TsL-11 sample.

The first reaction order with respect to ozone has been found at the initial step of the reaction of ozone decomposition over the SCWA-TsL-11 samples at the initial ozone concentration in the OAM ranging from 1 to 100 mg/m³. A deviation from the first reaction order in the case of half-reaction time is evidence of a chain-radical reaction mechanism. This agrees with the well-known conception of the ozone decomposition over individual metal oxides. The SCWA-TsL-11 sample provides air purification from ozone to the level less than MPCₖ₃ (0.1 mg/m³) at the initial ozone concentration of 1 mg/m³ (10 MPCₖ₃) for 140 min.
Физико-химические и каталитические свойства твердой составляющей сварочного аэрозоля

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Методами РФА, ИК-спектроскопии и рН-метрии охарактеризованы образцы твердой составляющей сварочного аэрозоля, образующегося при сварке стали электродом ЦП-11 (ISO E19.9NbB20). Фазы манганохромита, оксидов железа, марганца и никеля обусловливают каталитическое низкотемпературное разложения озона.

Ключевые слова: сварочный аэрозоль, твердая составляющая, определение характеристик, разложение озона, очистка воздуха

REFERENCES


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