Deep Oxidation of Fluorinated Hydrocarbons in Molten Catalysts

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Abstract

The oxidation of fluorine-containing organic substances: fluorocarbon liquid M-1, fluorinated alcohol $H(CF_2)_8CH_2OH$, and powder polytetrafluoroethylene with air has been studied in melts: NaOH; 43 mol.% LiCl − 33 mol.% NaCl − 24 mol.% KCl (eutectic mixture); (LiCl-NaCl-KCl)eutec. + 10 mass.% V_2O_5; (LiCl-NaCl-KCl) eutec. + 15 mass.% V_2O_5; 56 mol.% Na_2CO_3 − 44 mol.% K_2CO_3 (eutectic), (Na_2CO_3 − K_2CO_3)eutect. + 15 mass.% V_2O_5, and $K_3V_5O_{14}$.

The compositions of the melts have been examined by GC, DTA, chemical analysis and XRD, and they have been shown to change during the reaction, depending on the composition and partial pressure of the gaseous products over the melt surface. The alkali metal chloride melt containing 15 mass.% V_2O_5 has been found to be most stable to the action of fluorine compounds.

Possibility of deep oxidation of fluorine-containing organic substances in melts based on hydroxides, carbonates and chlorides of alkali metals doped with oxides of vanadium has been proved. The process of deep oxidation of fluorinated hydrocarbons is accompanied by formation of an equilibrium mixture containing hydroxides, carbonates, chlorides and fluorides of alkali metals, as well as their vanadates, if V_2O_5 additive is used. The relative amounts of these substances in molten systems are determined by the partial pressure of oxygen, CO_2 and water vapor.

Introduction

Halogenated hydrocarbons are used as solvents and feedstock for the synthesis of various materials, freons, and polymers. Perfluorinated hydrocarbons are widely adopted as lubricating oils, hydraulic fluids, and surfacants.

Burning of halogen-containing wastes is ecologically unacceptable because it yields more toxic substances, *e.g.*, dioxins [1].

For neutralization of fluorinated hydrocarbon waste, thermal destruction is traditionally used [2,3], however in this process fluorine compounds, such as hydrogen fluoride, are formed that should be removed from the gas stream before its discharge to the atmosphere. The process of thermal destruction of fluorinated hydrocarbons in the presence of oxides and hydroxides of alkali earth metals [3] prevents a release of halogens into the gas phase.

Melts composed of inorganic salts and metal ox-

ides are shown to catalyze processes of decomposition and oxidation of halogen-containing substances, including chemical agents [4,5]. According to the method described in ref. [6], halogen-containing organic wastes are treated in a bath with the melt consisting of an alkali-earth metal and an alkali-earth metal halogenide. The halogen formed upon waste combustion reacts with the metal. As a result, the alkali-earth metal halogenide is accumulated in the melt. It should be noted that the process is carried out at high temperature (>750°C) and requires an expensive alkali-earth metal to bind halogens.

Halogen-containing wastes can be destroyed in the sodium carbonate melt at 650-800°C [7]. It is noted that the resulting products (sodium halogenides) are relatively harmless, and the process has 30-40% lower cost than the conventional waste incineration with the subsequent scrubbing of the off-gas.

Previously [8], we reported that in the presence of oxygen chlorinated hydrocarbons undergo practically complete conversion in molten catalysts with

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predominant formation of products of deep oxidation. The present paper is devoted to the study of the conversion of fluorine-containing organic substances in the following melts: NaOH (**I**), 43 mol.% LiCl – 33 mol.% NaCl – 24 mol.% KCl (eutectic mixture) (**II**), (LiCl-NaCl-KCl) eutec. + 10 mass.% V_2O_5 (**III**), (LiCl-NaCl-KCl) eutec. + 15 mass.% V_2O_5 (**IV**), 56 mol.% Na_2CO_3 – 44 mol.% K_2CO_3 (eutectic.) (**V**), (Na_2CO_3 –K_2CO_3) eutect. + 15 mass.% V_2O_5 (**VI**) and $K_3V_5O_{14}$ (**VII**).

Experimental

The oxidation of organic substances in melts was studied in an experimental setup consisting of the following units: a vessel filled with organic substance, a pump, a bubble-type reactor placed in a furnace, a compressor for air supply to the reactor, a pressure reducer, a fine flow-regulating valve and a rotameter.

A mixture of air and an organic substance passes through a vertical feeding tube immersed in the melt to form an air-vapor mixture bubbling through the melt. The mixture undergoes chemical conversion in the melt, and the reaction products are either vented or directed to an absorption vessel filled with an aqueous solution of KJ, with starch added as an iodine indicator. The rotameter and the pump were calibrated for gas flow rates ranging from 25 to 80 l/h and liquid flow rates ranging from 0.01 to 0.2 l/h, respectively.

The reactor (240 mm long and 78 mm i.d.) is covered with a lid (60 mm thick) having a conical orifice to exclude 'dead space' (the principle of "ideal plug" operation). The free space of the non-operating reactor is ~50% of the melt volume. Because of changes in temperature and filling of the melt with the gas bubbles, the actual volume of the melt increases by ~35%. The remaining free space in the operating reactor is required to prevent the formation of the melt layer on the reactor lid caused by the entrainment of the melt droplets.

The reaction products were separated and analyzed by gas-liquid chromatography, using a 2.5 m column filled with SE-60 (15 mass.%) on Chromaton-N-AW support, at a temperature of 78°C.

CO_2, CO, N_2, and O_2 were analyzed by GC, using two consecutively connected columns. CO_2 was analyzed at 30°C using a column (3m long) filled with Polysorb-1. CO, N_2 and O_2 were separated at room temperature in a column (3 m long) filled with mo-

lecular sieve NaX.

Gas lines of two chromatographs were consecutively connected. Helium was used as gas carrier. The inlet pressure of the gas carrier was 2.2 kg/cm², and the gas flow rate at the outlet of the second analytical column was maintained at 24 cm³/min at atmospheric pressure. Katharometers were used for detecting the reaction components, at a detector current strength of 100 mA in the both GC instruments.

Concentrations of the gas mixture components were determined by the absolute calibration method. The calibration was performed by the introduction of gas samples into the GC by the dosing loop of a sampling valve and by injection of liquid samples with a micro-syringe.

The sampling of the air-vapor mixture at the reactor outlet was performed with a gas syringe preliminarily heated to 60-70°C to prevent condensation of liquid organic compounds. The sample volume was 1 cm³. The design of the GC analytical system provided complete analysis of the vapor-gas mixture from one sample.

The reagents used in the experiments were of "laboratory purity" grade.

Fluorinated alcohol $H(CF_2$-$CF_2)_4CH_2OH$ is a crystal powder, its melting temperature is 66-67°C. For convenient dosing, the alcohol was dissolved in chloroform and used as a solution (10 mass.%).

The fluorocarbon liquid M-1 corresponds to the Branch Standard 95-41976. The M-1 liquid is produced by fluorination of hydrocarbon oils. It is a lubricant used under aggressive media. It has a density of 1.9 g/cm³, and b.p. of 100-120°C at 400 Pa. It is insoluble in water and organic solvents. The thermal decomposition of M-1 begins at 300-400°C.

Polytetrafluoroethylene (PTFE) was dosed as fine powder suspended in air by passing air flow through a temperature-controlled vessel containing PTFE.*

An "ECOTEST" instrument supplied with ion-selective electrodes was used to measure concentrations of chlorine and fluorine in the off-gas. For this analysis, the off-gas was passed from the reactor through an aqueous potassium hydroxide solution (0.1 mol/l) for a specified period of time.

To reveal the presence of fluorine or chlorine in the reaction products, the off-gas was bubbled through an aqueous potassium iodide solution containing starch as a color indicator. The presence of fluorine was additionally confirmed by the fact that

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*The experiments on PTFE oxidation were performed by P.S.Dukhanin

the color of the iron sulfosalicylate complex solution changed from deep-cherry to light-yellow because of iron binding into a more strong fluoride complex. This reaction is used to determine fluorine by the colorimetrical method.

Results and Discussion

Polytetrafluorethylene oxidation in the NaOH melt was studied at 350 and 450°C. At these temperatures the complete oxidation of PTFE takes place. The off-gas contains nitrogen, water vapor and oxygen. The decrease of the concentration of oxygen in the off-gas compared to that in air corresponds to the amount of formed CO_2 that interacts with NaOH to yield sodium carbonate. CO_2 appears in the off-gas as the concentration of NaOH decreases due to formation of NaF and Na_2CO_3 during the reaction progress. The concentration of CO_2 in the off-gas sharply increases when the melt attains the following composition: 25 mass.% NaF, 40 mass.% Na_2CO_3, and 35 mass.% NaOH. A further change in the melt composition caused by accumulation of carbonate and fluoride anions results in a substantial increase of its viscosity.

PTFE is also completely oxidized in the $K_3V_5O_{14}$ melt (composition VII) at 500, 550, and 600°C. As the off-gas is passed through an aqueous KJ solution containing starch as an indicator, the solution takes on the color for a short time and then becomes colorless. After the addition of fresh potassium iodide solution, the color appears again. This phenomenon corresponds to the initial formation of iodine, which is then oxidized to iodate ion. A fresh portion of KJ provides formation of molecular iodine due to oxidation of iodide ion with fluorine in the reaction products.

According to XRD analysis of the fresh catalyst (composition VII) and the samples taken after 6, 12 and 24 h operation, the melt does not absorb the fluorine resulting from the PTFE oxidation. Potassium fluoride crystal phase was not detected in the samples, within detection limits of a DRON-3M diffractometer.

The fluorinated alcohol $H(CF_2)_8CH_2OH$ dissolved in $CHCl_3$ is completely oxidized in the above catalysts at >600°C.

Table 1 presents the data on the oxidation of M-1 liquid.

The concentration of CO_2 in the off-gas formed upon the oxidative destruction of M-1 in the melt Na_2CO_3-K_2CO_3 (V) at 600°C is 5.7 vol.%, which is a little higher than the calculated value (5.2 vol.%). The concentration of fluorine is 0.06 vol.%, which is considerably lower than the calculated value (10.4 vol.%). It is obvious that the fluorine or fluoride ion, resulting from the oxidative destruction of M-1, interacts with potassium and sodium carbonates to form alkali metal fluorides and to yield CO_2 into the gas phase. On further process progress, the concentration of CO_2 in the gas phase decreases to 4.8 vol.% (Table 1, run 2).

After the treatment of fluorocarbon liquid M-1 in the melt Na_2CO_3-K_2CO_3 (eutectic), the diffractograms of the melt indicate the presence of carbonates and fluorides of potassium and sodium.

The nitrogen/oxygen ratio in the off-gas is higher than that in air (3.77). When the melt is treated with air flow that does not contain fluorinated hydrocarbon vapors, the N_2/O_2 ratio in the off-gas is close to that in air (runs 3,5,7,9,10, and 12), and fluorine is not detected.

Addition of 15 mass.% V_2O_5 (VI) to the eutectic composition of potassium and sodium carbonates provides a release of CO_2 from the melt, which is indicated by the presence of CO_2 in the gas evolving from the reactor when air is blown into the melt and the fluorinated liquid is not supplied there (runs 3,5, 7,9,10, and 12 in Table 1). When air is passed through the potassium and sodium carbonate melt that does not contain V_2O_5, carbon dioxide is not observed in the off-gas.

It is known that the formal constant of Na_2CO_3 dissociation to CO_2 and Na_2O in the equimolar NaCl-KCl melt at 700°C is 0.4 when the melt is bubbled with dry oxygen [9]. The constant sharply decreases to 0.0012 (850°C) in the presence of CO_2 above the melt at atmospheric pressure [10]. Therefore, the observed CO_2 evolution can be explained by the decomposition of carbonates with added V_2O_5.

During the preparation of the reactor for experiments air is passed through the melt (VI). The resultant evolution of carbon dioxide from the melt is probably responsible for formation of potassium and sodium oxides. That is why the carbon dioxide and fluorine formed during the decomposition of M-1 are partially absorbed by the melt and their concentrations in the off-gas gas are below the calculated values.

In the case of the eutectic mixture of lithium, potassium and sodium chlorides (composition II), the off-gas does not contain fluorine and CO_2. At 450°C

Table 1

Composition of the products of M-1 liquid in different melts

No*	T, °C	O_2/M-1 over stoichiometry**	Composition of products in the gas phase, vol.% ***					
			N_2	O_2	N_2/O_2	CO_2	CO	F⁻, Cl⁻
Na_2CO_3-K_2CO_3 (eutect.)								
1	650	3.68	72	13.8	5.23	5.7	absent	0.06, -
2	700	3.68	72.5	15.0	4.8	4.8	absent	0.16, -
After experimental runs, the catalyst contains: Cl 0.16 mass.%, F 1.57 mass.% (a sample taken from the reactor middle); Cl 0.82 mass.% and F 0.98 mass.% (a sample taken from the reactor bottom) (Na_2CO_3-K_2CO_3) eutect. + 15 mass.% V_2O_5								
3	650	air	78	20.9	3.72	0.4	absent	- , -
4	650	3.05	77.1	18.1	4.25	1	traces	1.02, -
5	700	air	76.3	20.2	3.78	1.1	absent	- , -
6	700	3.05	78.2	15.2	5.1	2	traces	0.9, -
7	700	air	78	20	3.9	0.9	absent	- , -
8	700	3.68	77.8	17.2	4.5	1.4	traces	0.5, -
9	700	air	77.7	20	3.9	0.9	absent	- , -
10	650	air	76.8	20.8	3.7	traces	absent	- , -
11	650	3.68	77.7	18.1	4.3	1	traces	0.5, -
12	650	air	78	20.7	3.77	0.5	absent	- , -
LiCl-NaCl-KCl (eutect.)								
13	450	1.53	76.38	20.23	3.78	traces	absent	- , -
14	600	1.53	78.53	16.48	5	3	absent	- , -
(LiCl - NaCl - KCl) eutect. + 10 wt.% V_2O_5								
15	600	1.53	77.96	16.82	4.63	1.6	traces	- , -
16	600	3.05	77.80	17.1	4.55	1.3	traces	0.07, 0.4
(LiCl-NaCl-KCl) eutect. + 15 mass.% V_2O_5								
17	600	air	80.1	20.1	4.0	absent	absent	- , -
18	600	3.68	79.9	17.0	4.7	1.3	traces	0.4, 1.2
19	600	air	80.2	18.8	4.3	absent	absent	- , -
After experimental runs, the catalyst contains: Cl 18.77 mass.%, F 0.18 mass.%; the calculated initial Cl⁻ content is 54.4 wt.%								

* the runs are given in the order of their accomplishment;
** the stoichiometry relates to oxidation of M-1 with $(CF_2)_n$ composition to CO_2 and F_2;
*** data are averaged for two-three measurements;
"-" no data.

the ratio N_2/O_2 is 3.78 (equal to that of air) confirming that the fluorinated liquid is not noticeably oxidized under these conditions. At 600°C, the off-gas contains CO_2 and $N_2/O_2 = 5$ (run 15 in Table 1). The melt viscosity increases, probably due to the formation of potassium and sodium fluorides, which is indicated by thermogravimetrical measurements and XRD data.

The differential derivatogram curve of the eutectic mixture of lithium, sodium and potassium chlo-

rides shows an endothermic effect corresponding to the eutectic melting point (355°C) and small peaks corresponding to the melting points of the melt components (at ~610, 800 and 770°C). No weight loss is observed upon the sample heating up to 805°C. As the temperature is further increased from 805 to 960°C, the weight is reduced by 9 %.

Addition of 10 mass.% V_2O_5 to the melt II (forming the composition III) increases the molten catalyst lifetime. When air is passed through the melt without M-1 liquid, the outlet gas does not contain CO_2. The oxidation of M-1 is accompanied with the evolution of both chlorine and fluorine into the gas phase, moreover, their concentration increases if the amount of V_2O_5 in the melt increases (compare runs 18 and 20 in Table 1).

In our previous work [8], it was shown that the oxidation of $CHCl_3$ and CCl_4 in the melts of sodium and potassium carbonates containing V_2O_5 is accompanied by evolution of chlorine into the gas phase, which is the evidence of the oxidation of the formed chloride anions. The catalytic effect of phosphates on the oxidation of chloride anions in the sodium, potassium and calcium chlorides was observed in [11]. The interaction of V_2O_5 with alkali metal halogenides was studied in [12, 13]. The evolution of Cl_2 upon bubbling of ozone and carbon dioxide through the aqueous sodium chloride solution was observed in [14]. Chlorine also evolves due to the interaction of Na(K)Cl and V_2O_5 in the presence of oxygen [15, 16].

After oxidation of M-1 liquid in the catalyst LiCl-NaCl-KCl (eutec) + 10 mass.% V_2O_5 (III), the derivatogram of the catalyst exhibits numerous endothermic effects at 520-980°C, suggesting the presence of small amounts of chlorides, fluorides, carbonates and vanadates of alkali metals. On heating, the sample weight decreases by 3.3% at 415-480°C (a small mildly sloping exothermic peak), 3.3% at 480-890°C and ~6% at 820-980°C. A fresh sample begins to lose its weight at 400°C, the loss is 8.86% at a temperature range of 400-500°C. The concentration of carbonate ion in the spent catalyst is 10.4 mass.%.

As the concentration of V_2O_5 in the eutectic mixture of lithium, potassium and sodium chlorides is increased to 15 mass.% (IV), the temperature when the sample begins to lose its weight decreases to 210°C. The sample weight sharply decreases at 645°C. When the sample is heated to 1180°C, the total weight loss is 87.5%. On bubbling with M-1-

air mixture at 110-240°C, the catalyst (IV) loses about 14.8% of its weight, and the sample temperature slightly increases. For the temperature ranges 640-820 and 820-1190°C, the weight losses are 4.56 and 77.1%, respectively. When the temperature exceeds 820°C, a loss in the weight is accompanied by a sharp decrease in the sample temperature, which may be attributed to the beginning of either decomposition or evaporation of the catalyst components. Increasing the V_2O_5 concentration to 15 mass.%, facilitates the oxidation of chloride ions and release of chlorine into the gas phase, which increases the concentration of CO_3^{2-} in the catalyst to 15.5 mass.%.

Figures 1-3 present the observed accumulation of F^- in the carbonate melt (V) and NaOH-KOH (eutectic mixture) during M-1 oxidation, as well as the change of mass of F^- and CO_3^{2-} ions absorbed in KOH solution after passing the off-gas from the reactor.
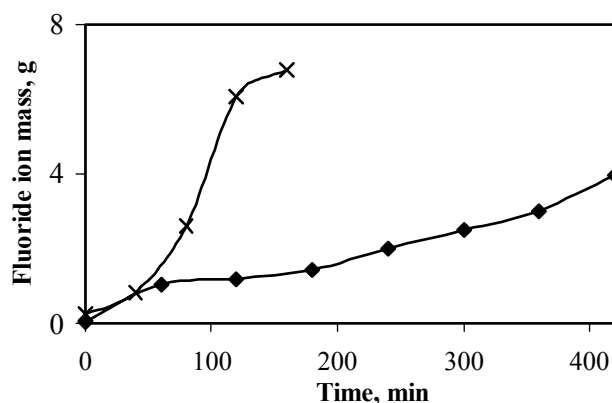

Fig. 1. Mass of fluoride ions accumulated in the melt *vs* time of M-1 oxidation, the rate of M-1 supply is 3 cm³/h, the rate of air supply is 25 l/h: ♦ - NaOH-KOH (400°C), ×- Na_2CO_3-K_2CO_3 (600°C)
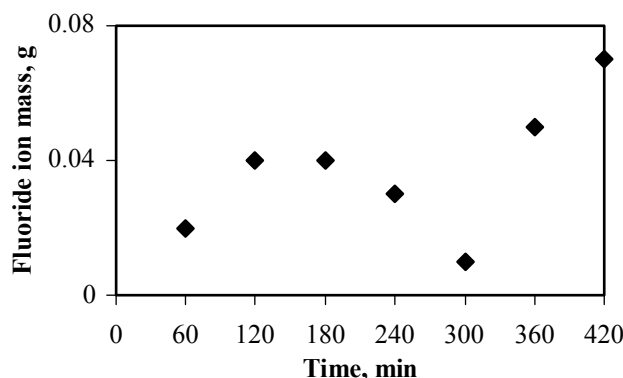

Fig. 2. Mass of fluoride ions absorbed in the aqueous KOH solution *vs*. time upon passing the reaction products of M-1 oxidation in NaOH-KOH melt (400°C), the supply rates of M-1 and air are 3 cm³/h and 25 l/h, respectively, at t = 300 min new portion of KOH solution was used.
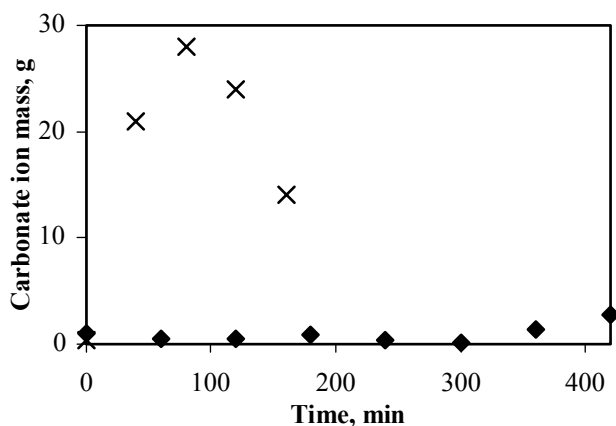
Fig. 3. Mass of carbonate ions absorbed in the aqueous KOH solution *vs.* time upon passing the reaction products of M-1 oxidation in melts, the supply rates of M-1 and air are 3 cm³/h and 25 l/h, respectively, at t = 300 min new portion of KOH solution was used: ♦ - NaOH-KOH (400°C), ×- Na_2CO_3-K_2CO_3 (600°C)

According to the obtained results, the melts and aqueous solution of KOH do not absorb the whole amount of fluorine found in the composition of M-1 liquid supplied to the reactor. For example, during the first hour of the M-1 oxidation in NaOH-KOH melt, only 1.06 g of fluoride ions were accumulated in the melt (Fig. 1) and 0.02 g of fluoride ions were absorbed by the KOH solution (Fig. 2). According to the calculations, 4.33 g of fluorine can be formed during 1 hour in the oxidation of 3 ml (5.7 g) of M-1. Certain part of the fluorine resulting from the oxidation of M-1 is likely to interact with quartz and alundum, which are construction materials of the bubble tube, the reactor and thermocouple wells.

When M-1 liquid is passed through the reactor for 40 min, the amount of CO_3^{2-} ions in the melt first increases and then begins to decrease. This can be explained by the fact that fluoride ions cause CO_2 evolution from potassium and sodium carbonates. As Fig. 3 shows, the concentration of carbonate ions in the aqueous KOH solution increases during passing the off-gas from the reactor containing NaOH-KOH.

Fluorine may evolve into the gas phase due to the oxidation of fluoride ions with oxygen in the presence of sodium and potassium metavanadates, as in the case of chloride ions [11-16]. The mechanism and kinetics of the reaction between atomic oxygen O (^{1}D) and CF_3Br yielding COF_2 and F_2 were studied in [17].

It should be taken into account that hydroxides and carbonates of alkali metals present in the melt form oxides, peroxides and superoxides of alkali metals under the reaction conditions [18, 19]. The presence of CO_2 in the reaction medium can promote the formation of fluorine from fluorides as was observed in ref. [14] for chloride ions, where chlorine was shown to form in the aqueous solution of NaCl under the action of ozone only in the presence of CO_2.

Conclusions

The results obtained prove the possibility of deep oxidation of fluorine-containing organic materials in melts based on hydroxides, carbonates and chlorides of alkali metals doped with oxides of vanadium and other metals with a variable valency. In all these systems, the process of deep oxidation of fluorinated hydrocarbons is accompanied by formation of the equilibrium mixture containing hydroxides, carbonates, chlorides and fluorides of alkali metals as well as their vanadates if V_2O_5 additive is used.

The ratio between the above substances in the molten system is determined by the partial pressures of oxygen, CO_2 and water vapor.

For this reason, perfluorinated hydrocarbons should be oxidized together with chlorinated hydrocarbons or, better still, with hydrocarbons which do not contain halogens. Such a combination of substances will provide the increased partial pressure of chlorine and CO_2 in the reactor, decreasing the probability of formation of high-melting alkali metal fluorides in the melt. One can alternate the treatment of fluorinated hydrocarbons and other organic substances. In this case, the fluorides resulting from the catalytic oxidation of fluorinated hydrocarbons can be partially converted into chlorides or carbonates, which will increase the lifetime of the catalysts.

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