

DETAILED KINETICS OF JET FUEL SURROGATES

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This work aims to present the capability of a detailed kinetic model to reproduce the oxidation of a jet fuel in conditions of both low and high temperatures. Because of the complexity of the fuel composition, the mixture is represented in terms of simple surrogate fuels constituted by mainly a linear (n-decane) and a branched (iso-octane) alkane and by an aromatic hydrocarbon (toluene). Two further surrogates include the presence of cycloalkanes: in one case cyclohexane and in the other case methylcyclohexane, in an amount ranging between 15 and 22 % (mole). Different operating conditions and different devices were experimentally investigated and theoretically simulated. The surrogates showed able to mimic the main ignition characteristics of the original jet fuel as well its reactivity. The kinetic mechanism reproduced well the main combustion properties and the ignition delay times in all the investigated conditions. Some deviations are still present in the prediction of some minor species.

1. INTRODUCTION

Gasoline, kerosene and diesel fuels are complex mixtures of thousands of chemical compounds, whose individual concentrations are often lower than 1% and, most of all, vary significantly from batch to batch, depending upon several factors including the parent crude oil, the season and the refinery process involved. Since complexity increases with the number of constituents, only a few studies have focused on the combustion aspects of complex mixtures of hydrocarbons. Recently, several studies examined complex hydrocarbon mixtures initially by selecting a limited number of possible reference components in order to experimentally reproduce the interesting properties of real fuels, such as the widely used JP-8 aviation fuel and/or other diesel and aviation fuels. [Lindstedt and Maurice, 2000; Violi et al., 2002; Montgomery et al., 2002; Agosta et al, 2004, Humer et al., 2007].

The detailed numerical simulation of the combustion of real fuels is only practical when applied to fuels which are mixtures of a limited number of components. These are the premises for the study of surrogate fuels. A surrogate is a mixture of only a few components able of emulating the combustion characteristics of the real fuel, with the advantage that the properties and the characteristics of the mixture are well defined and unchanging. Surrogate fuels are then very useful both for the design of more reproducible experimental tests and for the development of reliable kinetic models, which are always projected to a deeper understanding of combustion processes [Naik et al., 2005; Ranzi, 2006].

2. THE AVIATION FUEL POSF 4658 AND SURROGATE MIXTURES

Very recently Dooley et al. [2010] proposed three and four component jet fuel surrogates by simply reproducing the hydrogen/carbon ratio and derived cetane number of the target fuel. Mixtures of n-decane, iso-octane, toluene, cyclohexane and methyl-cyclohexane were considered to emulate the combustion properties of an actual aviation fuel, POSF 4658. The empirical formula of the fuel, determined experimentally with ASTM D5291, is $C_{10.17}H_{19.91}$ ($H/C = 1.957$). The Derived Cetane Number (DCN) is 47.1, and the threshold sooting index (TSI) is 21.4 [Dooley et al. [2010]. These data (DCN, H/C, TSI and the average molecular weight 142 g/mol) provided

the four constraints which were used to derive the surrogate mixtures. Table 1 reports the mole fractions of the three different proposed surrogate mixtures.

Table 1. Mole fractions of the three surrogate mixtures of POSF 4658 [Dooley et al., 2010]

	Surr_1	Surr_2	Surr_3
n-decane (n-C ₁₀ H ₂₂)	0.4267	0.482	0.422
iso-octane (i-C ₈ H ₁₈)	0.3302	0.175	0.174
Toluene (C ₇ H ₈)	0.2431	0.178	0.179
Cyclohexane (cy-C ₆ H ₁₂)	-	0.165	-
Methyl-Cyclohexane (CH ₃ -cy-C ₆ H ₁₁)	-	-	0.225

The validity of the proposed surrogate was evaluated by experimental measurement of select combustion properties of POSF 4658, and the POSF 4658 surrogate. Namely, the chemical reactivity and auto-ignition properties of stoichiometric mixtures in air of POSF 4658, and the POSF 4658 surrogate were investigated in the following systems:

- (1) A variable pressure flow reactor at 12.5 atm and 500–1000 K, with 0.3% C for both mixtures.
- (2) A shock tube at 674–1222 K and pressures close to 20 atm.
- (3) A rapid compression machine at 645–714 K at pressures close to 20 atm.

Finally, the strained extinction limit of diffusion flames were evaluated for measuring the high temperature reactivity and the kinetic-diffusion coupling of actual fuel and surrogate.

In this paper we analyze and compare the predictions of a general kinetic scheme of fuel combustion with all the experimental measurements, including the recent n-dodecane shock tube experiments of Davidson et al (2011).

3. KINETIC MODEL AND NUMERICAL METHODS

The semi-detailed oxidation mechanism of hydrocarbons up to C16 adopted herein [Ranzi et al., 2011], consisting of over 10000 reactions and 350 species, was developed based on hierarchical modularity and lumping procedures. The kinetic modeling of the pyrolysis and oxidation of large hydrocarbon molecules is very complex, both for the huge number of elementary reactions involved and for the number of intermediate species required for describing successive reactions. Thus, a well balanced kinetic model requires the correct selection of the relevant reactions of these intermediates, typically alkenes, cyclic ethers, aldehydes, ketones, and so on. To reduce this complexity, a proper lumping approach, with extensive use of analogy rules, could facilitate progress making more viable and flexible the extension of the overall kinetic scheme toward new heavy reference components. The lumped approach reduces the overall complexity of the resulting kinetic scheme, both in terms of equivalent species and lumped or equivalent reactions. The lumped scheme first refers to a simplified description of the primary propagation reactions of large species, then treats successive reactions of smaller intermediate species with a detailed kinetic scheme.

Thermochemical data for most species were obtained from the CHEMKIN thermodynamic database [Kee et al., 1983]. For those species whose thermodynamic data are not available in the literature, the group additive method was used to estimate these properties. The complete mechanism, with thermodynamic and transport properties, is available in the CHEMKIN format [<http://creckmodeling.chem.polimi.it>].

Laminar flame speeds were calculated for the steady-state, freely propagating, adiabatic flames in the doubly infinite domain, with negligible viscosity, body force, and radiative heat transfer while allowing for Soret diffusion. The conservation equations with proper boundary conditions were discretized by means of conventional finite differencing techniques with non-uniform mesh spacing. Diffusive terms use central differences while convective terms use upwind differencing for better convergence.

4. MODEL PREDICTIONS AND COMPARISONS WITH EXPERIMENTAL MEASUREMENTS

A detailed description of all the different experimental devices and related operating conditions are given in Dooley et al. [2010].

4.1 Variable pressure flow reactor

The reactivity of both POSF 4658 and surrogate were determined over the temperature range, 500–1000 K, fixed reaction time (1.8 s) and constant pressure (12.5 atm). Measurements of oxygen, carbon dioxide, carbon monoxide, and water mole fractions and heat release (ΔT) as a function of initial feed temperature allowed a proper comparison of the kinetic behavior of the two fuels at low and hot ignition temperatures.

The first set of data refers to n-decane oxidation. n-decane is always the most abundant component of the surrogate mixture (table 1) and the most reactive in the low temperature region. Its study allows then a proper understanding of the autoignition and of the NTC behavior.

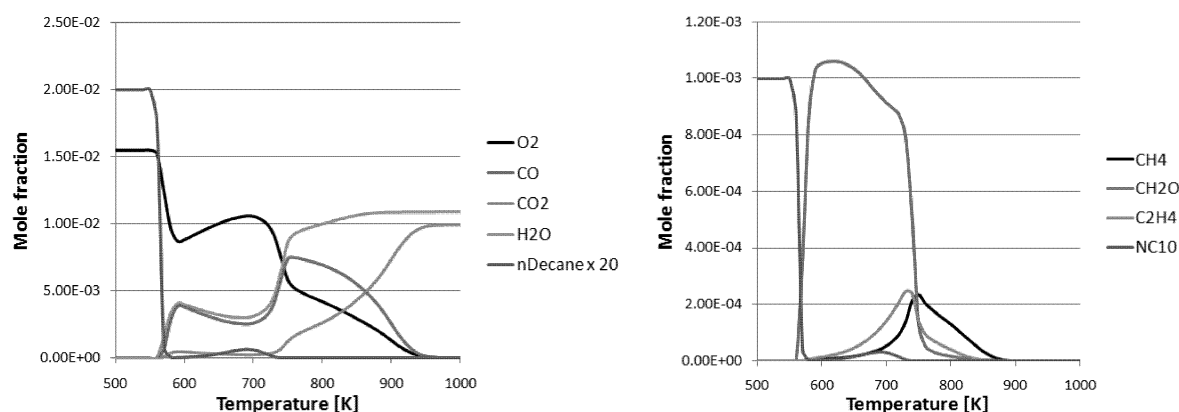
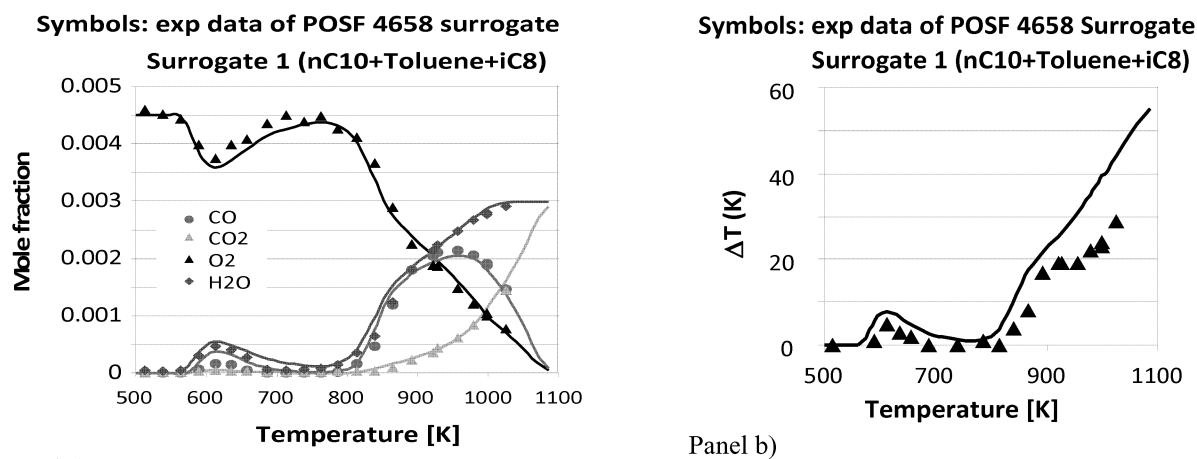


Fig. 1 - Flow reactor n-decane oxidation data for conditions of 12.5 atm and $s = 1.8$ s (n-decane 1000 ppm, O₂ 15500 ppm in N₂): POLIMI kinetic model (solid lines). Panel a) mole fractions of O₂, CO, CO₂ and H₂O versus initial feed temperature. Panel b) mole fractions of CH₄, C₂H₄ and CH₂O.



Panel a)

Panel b)

Fig. 2 - Flow reactor oxidation data for conditions of 12.5 atm and $s = 1.8$ s, for POSF 4658 surrogate (symbols) and POLIMI kinetic model (solid lines). Panel a) mole fractions of O₂, CO, CO₂ and H₂O versus initial feed temperature. Panel b) ΔT versus initial feed temperature.

Fig. 1 shows the simulation results. The experimental data are not shown since they are not published yet (we thank Dr. Saeed Jahangirian of Princeton University for the availability of the data prior to publication). The low and high temperature ranges, as well as the NTC zone can be observed. The agreement in terms of the overall reactivity in the whole range of conditions is very good, only at temperatures below 550 K the reactivity is under-estimated. In these conditions the reactions between peroxy radicals with O_2 depletion can play a role. At the same time, these reactions are not accounted for in the mechanism, because the kinetic model is not expected to be used at these very low temperatures. CH_4 formation is well predicted by the model, while CH_2O is overestimated. At the same time, ethylene formation is not properly captured by the model. Further research activity is required to better define the reasons of the observed deviations in the low temperature and NTC regions.

Symbols: exp data of POSF 4658 Surrogate

Lines: Surrogates

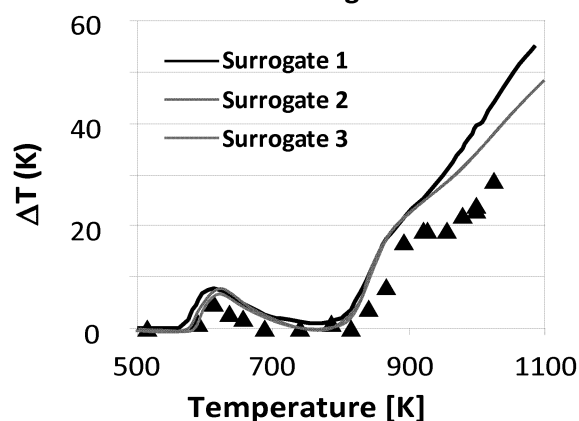


Fig. 3 - Flow reactor oxidation data for conditions of 12.5 atm and $s = 1.8$ s, for POSF 4658 (solid symbols) and POLIMI kinetic model (lines). Adiabatic ΔT versus initial feed temperature

In the case of surrogates, carbon concentrations of 0.3 mol.% were utilized in both real fuel and surrogate mixture experiments. The predictions of the kinetic model and the comparisons with the detailed measurements allow an analysis of the chemical processes which affect the overall fuel reactivity in the different conditions. Figure 2 shows the comparisons between model predictions and experimental measurements for POSF 4658 surrogate. A very accurate agreement in the whole range of conditions can be observed. Two minor points could be raised: a slightly higher predicted reactivity in the negative temperature region (NTC) and an overestimation of the adiabatic temperature increase at high temperatures.

This deviation is common to all the comparisons carried out in the variable pressure flow reactor and can be partially explained with the transfer and flow properties of the mixture. Figure 3 compares the adiabatic ΔT for the actual fuel POSF 4658 with the model predictions for the three surrogates. Both surrogate mixtures 2 and 3, containing cyclohexane and methyl-cyclohexane, reduce the over prediction of the heat release at high temperatures. Furthermore, the low temperature reactivity (550–700 K) seems to be very similar for the three surrogate mixtures.

4.2 Shock tube

The ignition behavior of both POSF 4658 and its surrogate was also studied at pressures of ~ 20 atm and shock temperatures of 650–1200 K. Figure 4 (panel a) first shows the agreement between the ignition delay times of POSF 4658 and its surrogate, then also shows that predicted ignitions of surrogate fairly agree with the corresponding experimental measurements. In these conditions the NTC region is located between about 800 and 950 K. Furthermore, panel b) of the same figure shows that model predictions of the three surrogates behave in a very similar way, all in quite close agreement with measurements.

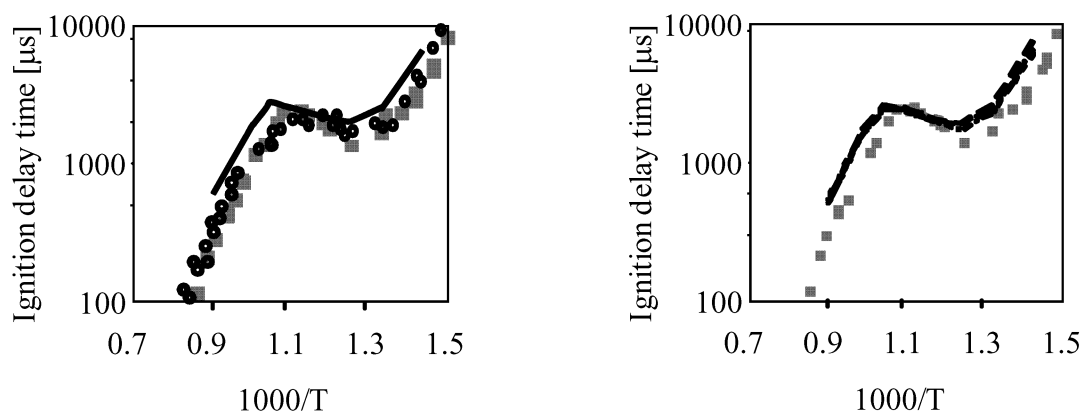


Fig. 4. Panel a) Ignition delay times for POSF 4658 (circles), POSF 4658 surrogate, (squares) and model predictions for surrogate 1 at 20 atm (line). Panel b) Ignition delay times for POSF 4658 surrogate, (symbols) and model predictions for the three surrogates at 20 atm (lines).

Davidson et al. [2011] measured the concentration time-histories behind reflected shock waves during n-dodecane oxidation for five species: n-dodecane, C_2H_4 , OH, CO_2 , and H_2O . Experiments were conducted at temperatures of 1300–1600 K and pressures near 2 atm, using mixtures of 400 ppm n-dodecane and 7400 ppm oxygen ($\phi = 1$) in argon. Figure 5 shows the comparison between model predictions and experimental data. N-dodecane measurements are not available, therefore the comparison is made using measurements for n-dodecane, which is also a component of several jet fuels surrogates [Humer et al., 2007] [Ranzi et al., 2006]. It is possible to observe that not only the fuel consumption is well predicted by the model but also the formation of OH radical and ethylene is in very good agreement with the experimental data.

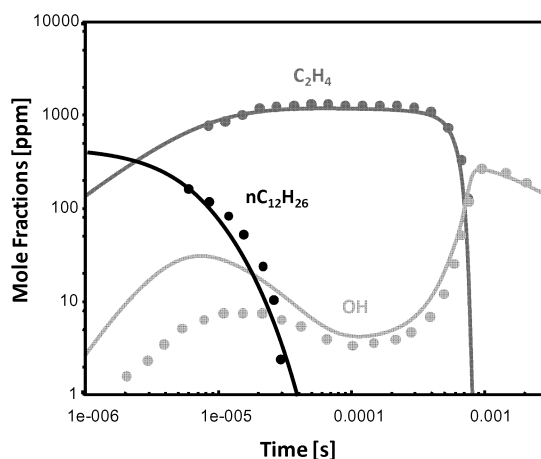


Fig. 5. Species time-histories for ndodecane, OH and C_2H_4 . Points: experiments. Lines: simulations. Initial reflected shock conditions: 1410 K, 2.37 atm, 457 ppm n-dodecane, 7577 ppm O_2/Argon

4.3 Rapid compression machine

A heated RCM was used to obtain ignition delay measurements of both POSF 4658 and its surrogate fuel at 22.3 atm over the compressed temperature range 639–721 K. Again, Figure 6 confirms a very close agreement not only of the two fuels but also the similar predicted ignition delays for the three surrogates.

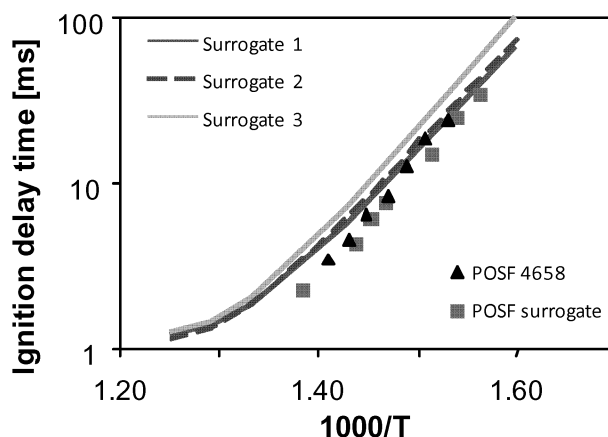


Fig. 6. RCM measurements and simulations. Ignition delay times for POSF 4658 16.3–24.8 atm (triangles), POSF 4658 surrogate 17.7–22.9 atm (squares) and model simulation of the three surrogates (lines).

These conditions are typical of the low temperature region and the reactivity is then controlled by the peroxide formation and from the branching of ketohydroperoxides in particular. Despite the quite long ignition delay, the comparison between model and experimental data seems show a negligible heat transfer effect of the compression stage of the device.

4.4 Extinction limits of diffusion flames

Figure 7 shows the comparison between model predictions and extinction experimental data in a counterflow flame [Dooley et al., 2010]. They used a counterflow burner to measure the extinction strain rate as a function of nitrogen dilution for POSF 4658 and the proposed POSF 4658 surrogate for diffusion flames. The temperature of the fuel side was maintained at 500 ± 5 K, and that of the oxidizer (air) side at $298 \text{ K} \pm 2$ K. Flame extinctions were calculated with 225 grid points. The numerical procedure adopted to calculate the extinction limit is described in greater detail in [Humer et al., 2007].

It is possible to observe that the model is able to correctly predict the extinction strain rate at low values of the fuel mole fraction in the fuel/ N_2 mixture, while underpredicts the experimental data by up to 15% at higher mole/mass fractions. A similar deviation was already observed by Dooley et al. [2010], using a different kinetic mechanism.

It is also interesting to compare the results of the numerical simulation with the experimental data of Hummer et al. [2007] obtained in the same experimental conditions, but using different Jet Fuels. Figure 8 shows the comparison between model results and experimental data. The measured extinction strain rates of the POSF4658 generally agree with the previous Jet-A and JP8 measurements of Hummer et al. [2007], but a deviation can be observed at high fuel concentrations.

As already observed by Dooley et al. [2010], when the extinction data are analyzed in terms of fuel mass fraction, there is a significant difference between POSF 4658 and the Jet fuel surrogate. This deviation is associated to the lower average molecular weight of the surrogate compared to that of POSF 4658. A sensitivity analysis was performed to check the possible effect of diffusion coefficients used for the fuel species on the

extinction predictions. This analysis showed that in these conditions this effect is not large and therefore the observed deviation cannot be simply related to uncertainties in the diffusion properties used.

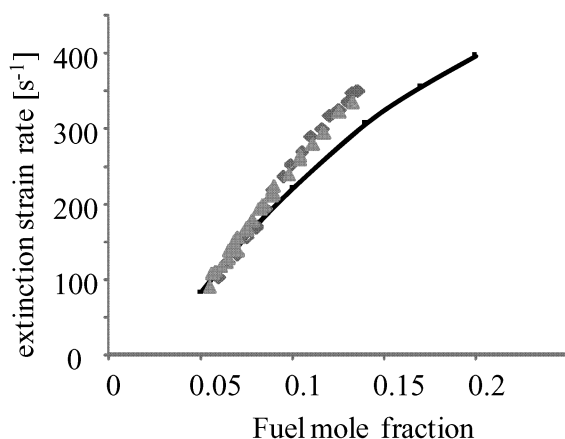


Fig. 7. Extinction train rates for counter flow diffusion flames at 1 atm, POSF 4658 (triangles), POSF 4658 surrogate (diamonds) and POSF 4658 model simulation (line).

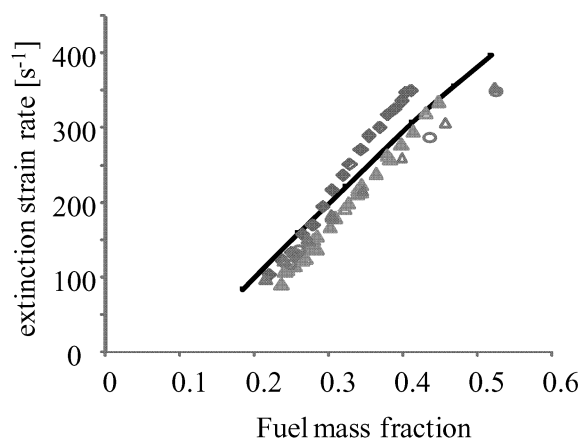


Fig. 8. Extinction Strain rates for counter flow diffusion flames at 1 atm. POSF 4658 (triangles), POSF 4658 surrogate (diamonds) Jet-A (empty triangles) and JP8 (empty circles) data of Humer et al [2007]. POSF 4658 surrogate model simulation (line).

5. COMMENTS AND CONCLUSIONS

Simple mixture of surrogate fuels demonstrate able to mimic the behavior of the complex mixture of aviation fuels in very wide ranges of operating conditions. Different surrogate mixtures were proposed all based on mainly a linear (n-decane) and a branched (iso-octane) alkane and by an aromatic hydrocarbon (toluene). Two further surrogates include the presence of cycloalkanes: in one case cyclohexane and in the other case methylcyclohexane, in an amount ranging between 15 and 22 % (mole). Experimental data carried out in a shock tube and a rapid compression machine at pressure between about 18 and 23 atm, temperature ranges between 650 and 1250 K showed very similar autoignition between the real fuel and its surrogate.

A detailed kinetic mechanism previously developed was further validated in comparison with this new set of data. The ignition delay times were properly predicted and found to be mostly unaffected by the surrogate mixture composition. The surrogate was also oxidized in a variable pressure flow reactor at a pressure of 12.5 atm and in a temperature range between about 500 and 1100 K. The model reproduced very well the reactivity of the system in these conditions, particularly identifying the correct position and value of the low temperature mechanism. Main product were also well predicted. The extinction limits in flames are also satisfactorily predicted by the model.

6. ACKNOWLEDGMENTS

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