# Comparative ballistic efficiency of solid composite propellants: which energetic plasticizer/polymer combination is the energetically preferred binder?

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**Experimental part**

For a wide variety of energetic compounds, data on enthalpies of formation, $\Delta H^0_f$, and densities, $d$, have been published. However, the data given in different sources often differ significantly. To select the most reliable data on the enthalpies of formation, the experimental values from different sources were compared with the calculated values estimated using the energy contributions to the enthalpy of formation in the liquid[S1] or solid state[S2] of the groups that make up the plasticizer or polymer.

The preference was given to the experimental values closest to the calculated ones. In the absence of experimental data, the calculated data were used. In this case, the calculation was based on the reliably determined $\Delta H^0_f$ values for compound-analogs with the subsequent replacement of the energy contributions of the changing groups.

For SCP, the specific impulse $I_{sp}$ is the main parameter characterizing the energetic performance. It was calculated at pressures in the combustion chamber of 4.0 MPa and at the nozzle exit of 0.1 MPa. The calculations were performed basing on known[S2] the TERRA Code. This software, based on the consideration of high-temperature chemical equilibria, is widely used to evaluate the theoretical performance of various propellant compositions.[S3]

To compare the ballistic efficiency of propellant formulations with different densities, when they are used in engines with different volume-mass characteristics, we used so-called effective impulses $I_{ef}(3)$ at the third stage of multi-stage rocket systems.
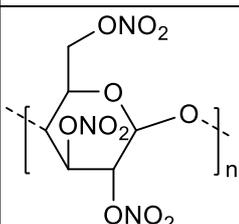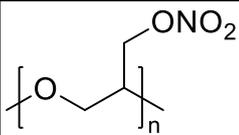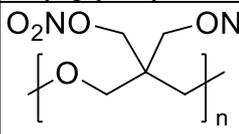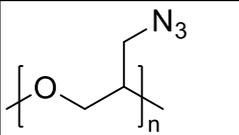
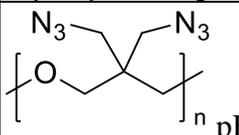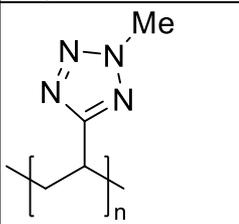$I_{ef}(3) = I_{sp} + 25(d - 1.7)$,
where $d$ is the density of the composition, g cm$^{-3}$.

In this report, we evaluate the ballistic performance of propellants for the third stage of the multi-stage rocket system. The possibility of using the described compounds in the near future at the lower stages, where the mass of the propellant is tens of tons, is still unlikely. In addition, compositions with aluminum hydride have insufficient density, which makes them not very profitable in the lower stages.

Statistical analysis was performed using the gradient descent method or steepest descent method[S4] using the SygmaPlot code. This technique is usually used to determine the empirical dependencies of multiparameter systems,[S5] when, with a relatively small number of objects under study (even with ten), quantitative patterns (if any, in principle, exist) of the dependence of the objective function on the selected parameters are already clearly traced.[S6]

**Table S1**. Properties of energetic polymers of this study

| NN | Structure of a unit, name (Code) | Formula of the unit | $\alpha^*$ | $d/$ g cm$^{-3}$ | $\Delta H^o_{f.}/$ kJ mol$^{-1}$ | $\Delta H^o_{f.}/$ kJ kg$^{-1}$ |
|---|---|---|---|---|---|---|
| **P1** |  Cellulose nitrate (NC) | $C_6H_7N_3O_{11}$ | 0.71 | 1.66 | -658.1[6] | -2234 |
| **P2** | [–CH$_2$CH(ONO$_2$)–]$_n$ Poly(vinyl nitrate) (PVN) | $C_2H_3NO_3$ | 0.54 | 1.5 | -144.77[S1] -149.8$_{calc}$ | -1626 |
| **P3** |  Poly(glycidyl nitrate) (PGN) | $C_3H_5NO_3$ | 0.35 | 1.46 | -284.09[S2] -284.9$_{calc}$ | -2385.8 |
| **P4** |  (pBNMO) Poly(bisnitratomethyloxetane) | $C_5H_8N_2O_7$ | 0.5 | 1.54 | -450.6$_{calc}$ | -2165.0$_{calc}$ |
| **P5** | [–CH$_2$CH(N$_3$)–]$_n$ Polyvinylazide | $C_2H_3N_3$ | 0 | 1.18 | 283.7$_{calc}$ | 4111.6$_{calc}$ |
| **P6** |  Glycidyl azide polymer (GAP) | $C_3H_5N_3O$ | 0.12 | 1.29 1.3 | 142.26[S7] 175.73[S8] 160.2$_{calc}$ | 1436 1773 1616.7$_{calc}$ |
| **P7** |  pBAMO Poly(bis(azidomethyl)oxetane) | $C_5H_8N_6O$ | 0.07 | 1.29 | 468.51[S9] 460.7$_{calc}$ | 2786 |
| **P8** |  Polyvinylmethyltetrazole | $C_4H_6N_4$ | 0 | 1.28 | 216.73[S10] | 1968 |

For polymers **P4** and **P5**, the enthalpies of formation were calculated in this work

**Table S2**. Some properties of oxygen-rich plasticizers of this study

| NN | Structure and name | Formula (Mw) | M.p./ °C | $d$/ g cm$^{-3}$ | $\Delta H°_f$, kJ mol$^{-1}$ (kJ kg$^{-1}$) | $\alpha$ | %H |
|---|---|---|---|---|---|---|---|
| **L1** | 3,4-Dinitrofurazan (DNF) | $C_2N_4O_5$ (160.045) | -15 | 1.62 | 235.14[S11] (1471.3) | 1.25 | 0 |
| **L2** | Trinitromethane $CH(NO_2)_3$ | $CHN_3O_6$ (151.03) | 26 | 1.47 | -45.1[S12] (-298.6) | 2.4 | 0.66 |
| **L3** | Tetranitromethane $C(NO_2)_4$ | $CN_4O_8$ (196.033) | 14 | 1.64 | +38.00[S12] (+193.8) | 4 | 0 |
| **L4** | Ethylene glycol dinitrate (EGDN) $O_2NOCH_2CH_2ONO_2$ | $C_2H_4N_2O_6$ (152.064) | -22 | 1.49 | -242.76[S13] (-1596) | 1 | 2.6 |
| **L5** | Nitroglycerol (NG) $O_2NOCH(CH_2ONO_2)_2$ | $C_3H_5N_3O_9$ (152.064) | 13 | 1.59 | -370.70[S13] (-1632) | 1.06 | 3.3 |
| **L6** | Diethylene glycol dinitrate (DEGN) $O(CH_2CH_2ONO_2)_2$ | $C_4H_8N_2O_7$ (196.12) | 2 | 1.385 | -418.99[S14] (-2136) | 0.58 | 4.1 |
| **L7** | 3,4-Bis(nitroxymethyl)furazan | $C_4H_4N_4O_7$ (220.097) | -6 | 1.57 | -47.7[S15] (-216.7) | 0.7 | 1.8 |
| **L8** | 3,5-Bis(nitroxymethyl)-isoxazole IDN | $C_5H_5N_3O_7$ (219.109) | -76 | 1.494 | -214.7calc* (-979.8) | 0.67 | 2.28 |
| **L9** | 5,5'-Bis(nitroxymethyl)bi-3,3'-(1,2,4-oxadiazole) | $C_6H_4N_6O_8$ (288.132) | 84.5 | 1.832 | -62.6calc* (-275.6) | 0.57 | 1.4 |
| **L10** | 5,5'-Bis(nitroxymethyl)bi-3,3'-(isoxazole) BIDN | $C_8H_6N_4O_8$ (286.156) | 92 | 1.585 | -183.1calc* (-639.9) | 0.42 | 2.1 |
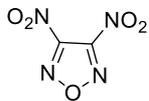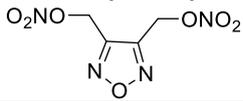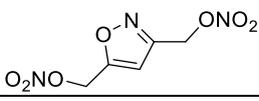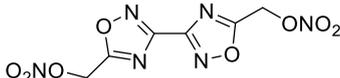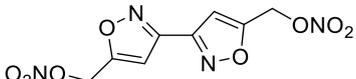
* For plasticizers **L10**-**L12**, $\Delta H°_f$ are calculated in this work

# Enthalpies of formation, $\Delta H^0_f$

Polymer **P2**: The calculated and experimental enthalpies of formation are close; therefore, the latter is recommended for use in calculations.

Polymer **P3**: The calculated and experimental enthalpies of formation are almost identical; the latter is recommended for use in calculations.

Polymer **P6**: The calculated value of the enthalpy of formation is close to the arithmetic mean of the two previously published, so it was used in this study.

Polymer **P7**: The calculated and experimental enthalpies of formation are close; therefore, the latter is recommended for use in calculations.

Calculated values of enthalpies of formation for plasticizers **L8** ($\Delta H°_f$ = -45.8 kJ mol$^{-1}$, Ref.[S16]), **L9** ($\Delta H°_f$ = -79.4 kJ mol$^{-1}$, Ref.[S17]) and **L10** ($\Delta H°_f$ = -139 kJ mol$^{-1}$, Ref.[S18]), given in the
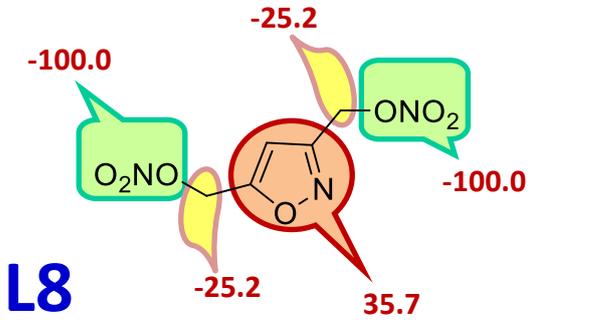
literature are questionable. For example, the experimental $\Delta H^{\circ}_f$ for 3,5-dimethylisoxazole is -63.1 kJ mol$^{-1}$ (Ref.[S15]). Since the contribution of the nitroxymethyl group to the enthalpy of formation is -125.2 kJ mol$^{-1}$ (Ref.[S19]), it is obvious that **L8** plasticizers should have a significantly lower $\Delta H^{\circ}_f$ than 3,5-dimethylisoxazole.

The contribution to $\Delta H^{\circ}_f$ of the isoxazole unit, estimated based on the $\Delta H^{\circ}_f$ of 3,5-dimethylisooxazole and the contribution of the methyl group (-49.37 kJ mol$^{-1}$)[S19], is:

$$\Delta\Delta H^{\circ}_f = -63.09 - 2\times(-49.37) = 35.7 \text{ kJ mol}^{-1}$$

The contribution of the 1,2,4-oxadiazole unit, based on $\Delta H^{\circ}_f$ of 3-phenyl-5-methyl-1,2,4-oxadiazole (104.18 kJ mol$^{-1}$)[S20] and the contribution of the methyl and phenyl groups,[S21] is equivalent to 95.9 kJ mol$^{-1}$. Thus, the contribution of the 1,2,4-oxadiazole unit is greater than that of the isoxazole unit by *ca*. 60 kJ mol$^{-1}$.

A visual representation of group additivity values and estimating the enthalpy of the formation of selected plasticizers using the contribution of groups in the liquid for **L8** and solid state for **L9** and **L10**[S21,S21] is shown in Figure S1.
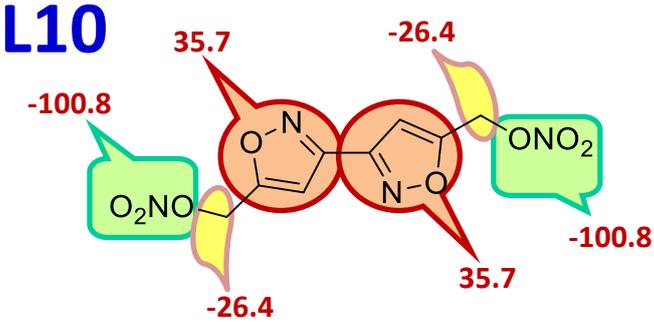


**Figure S1** Enthalpies of formation for plasticizers **L8**, **L9** and **L10**

**Table S3**. $I_{sp}$ values of 80 formulations containing 25% $AlH_3$, 50% ADN, 20% plasticizer **L1-L12**, and 5% polymer **P1-P8**.

| Plasticizer | Polymer | | | | | | | | Average for all polymers |
|---|---|---|---|---|---|---|---|---|---|
| | **P1** | **P2** | **P3** | **P4** | **P5** | **P6** | **P7** | **P8** | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| **L1** | 276.7 | 278.0 | 277.5 | 277.5 | 279.2 | 278.6 | 279.1 | 278.3 | **278.1** |
| **L2** | 277.0 | 277.0 | 276.6 | 276.4 | 278.4 | 277.9 | 278.2 | 277.8 | **277.4** |
| **L3** | 276.6 | 276.7 | 276.3 | 276.0 | 278.3 | 277.7 | 278.1 | 277.7 | **277.2** |
| **L4** | 277.8 | 277.4 | 277.0 | 276.9 | 278.5 | 278.0 | 278.3 | 277.6 | **277.7** |
| **L5** | 277.0 | 276.6 | 276.2 | 276.2 | 277.8 | 277.2 | 277.6 | 276.8 | **276.9** |
| **L6** | 277.4 | 276.6 | 276.1 | 276.4 | 277.5 | 277.0 | 277.3 | 276.4 | **276.9** |
| **L7** | 278.7 | 278.0 | 277.6 | 277.7 | 279.0 | 278.5 | 278.9 | 277.9 | **278.3** |
| **L8** | 275.9 | 274.7 | 274.1 | 274.8 | 276.0 | 275.4 | 275.8 | 274.7 | **275.2** |
| **L9** | 275.5 | 274.6 | 274.2 | 274.5 | 275.5 | 275.0 | 275.4 | 274.3 | **274.9** |
| **L10** | 275.2 | 274.3 | 273.8 | 274.1 | 275.1 | 274.6 | 274.9 | 274.0 | **274.5** |
| Average for all plasticizers | **276.8** | **276.4** | **275.9** | **276.1** | **277.5** | **277.0** | **277.4** | **276.6** | |

Obviously, with a fixed binder content (20% plasticizer and 5% polymer), a decrease in the percentage of oxygen in the polymer requires its growth in the plasticizer. To increase $I_{sp}$ by 0.5 s, the percentage of hydrogen by 0.85 abs% must be increased, either $\alpha$ by 0.54, or $\Delta H^0_f$ by ~250 kJ kg$^{-1}$ with the remaining characteristics constant.

**Table S4**. Values of $k_0$ - $k_3$ of the equation (1)

| $k_i$ | **P1** | **P2** | **P3** | **P4** | **P5** | **P6** | **P7** | **P8** | average |
|---|---|---|---|---|---|---|---|---|---|
| $k_0$ | 274.6 | 273.12 | 272.7 | 273.1 | 274.0 | 273.6 | 273.9 | 272.9 | 273.5 |
| $k_1$ | 1.05 | 1.75 | 1.71 | 1.66 | 1.73 | 1.66 | 1.74 | 1.70 | 1.63 |
| $k_2$ | 0.57 | 1.03 | 1.04 | 0.83 | 1.21 | 1.17 | 1.19 | 1.38 | 1.05 |
| $k_3$ | 0.000858 | 0.0020 | 0.00194 | 0.00190 | 0.00197 | 0.00190 | 0.00202 | 0.00194 | 0.00181 |

The last column of Table S4 shows the average values of the $k_0$-$k_3$ coefficients for the eight polymers. The deviation of the values calculated using TERRA code from those calculated by equation (1) using the coefficients from column 10 of Table S3 is about 1 s. The calculated averaged values $k_1$-$k_3$ roughly characterize the quantitative effect of the characteristics of the plasticizer, such as the percentage of hydrogen (%H), $\alpha$ and the enthalpy of formation ($\Delta H^0_f$), on the $I_{sp}$ value of the model composition (25% $AlH_3$, 50% ADN, 20% plasticizer, and 5% polymer). For example, the $k_2$ values, correcting the contribution of the oxygen content in polymer, for the different polymers range from 0.6 to 1.4. As shown in Figure S2 for these polymers, the dependence of $k_2$ on the value $\alpha$ of polymers is close to linear; $k_2$ increases with decreasing value of $\alpha$.
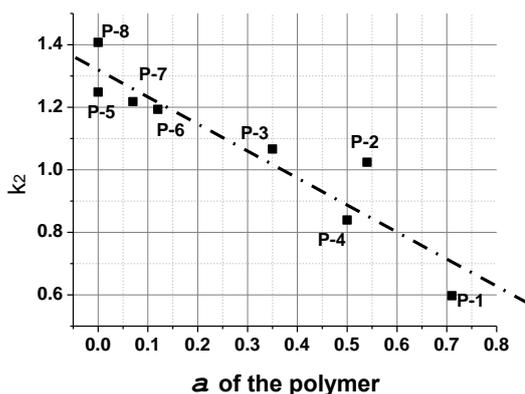
**Figure S2.** Dependence of the $k_2$ value (equation 1) on the α value of the polymer

As noted above, it is convenient to use the $I_{ef}(3)$ values to compare the ballistic efficiency of different formulations. Here it is the most interesting to estimate $I_{ef}(3)$, where the densities of the individual components and, therefore, of the final composition are important. The $I_{ef}(3)$ values characterizing the relative ballistic efficiency of the propellants at the upper stage are summarized in Table S5.

**Table S5** $I_{ef}(3)$ values computed using the TERRA Code for model SCP containing 25% $AlH_3$ + 50% ADN + 5% polymer **P1-P8** + 20% plasticizer **L1-L12**.

| Plasticizer | Polymer | | | | | | | | |
|:---:|:---:|:---:|:---:|:---:|:---:|:---:|:---:|:---:|:---:|
| | **P1** | **P2** | **P3** | **P4** | **P5** | **P6** | **P7** | **P8** | Average for all polymers |
| | $I_{ef}(3)$ | | | | | | | | |
| **L1** | 276.1 | 277.1 | 276.6 | 276.7 | 277.7 | 277.4 | 277.8 | 277.1 | 277.1 |
| **L2** | 274.2 | 275.3 | 274.8 | 274.7 | 276.1 | 275.8 | 276.1 | 275.7 | 275.3 |
| **L3** | 274.7 | 275.9 | 275.5 | 275.3 | 276.9 | 276.6 | 276.9 | 276.6 | 276.1 |
| **L4** | 275.1 | 275.8 | 275.3 | 275.4 | 276.3 | 276 | 276.3 | 275.6 | 275.7 |
| **L5** | 274.9 | 275.6 | 275.1 | 275.2 | 276.2 | 275.8 | 276.2 | 275.4 | 275.6 |
| **L6** | 274.1 | 274.3 | 273.8 | 274.2 | 274.7 | 274.4 | 274.7 | 273.8 | 274.3 |
| **L7** | 276.5 | 276.9 | 276.4 | 276.6 | 277.3 | 277 | 277.4 | 276.4 | 276.8 |
| **L8** | 273.2 | 273.1 | 272.5 | 273.3 | 273.8 | 273.5 | 273.8 | 272.8 | 273.3 |
| **L9** | 274.5 | 274.8 | 274.3 | 274.7 | 275 | 274.8 | 275.1 | 274.1 | 274.7 |
| **L10** | 273 | 273.2 | 272.7 | 273.1 | 273.4 | 273.2 | 273.5 | 272.6 | 273.1 |
| Average for all plasticizers | 274.6 | 275.2 | 274.7 | 274.9 | 275.7 | 275.5 | 275.8 | 275.0 | |

For clarity, a comparison can be made on a small group of plasticizers. Figure S3 shows the values of $I_{ef}(3)$ of compositions based on four plasticizers: (i) tetranitromethane (**L3**) with the highest α = 4.0 at $\Delta H^0_f$ = +196 kJ kg$^{-1}$; (ii) 3,4-dinitrofurazan (**L1**) with α = 1.25 and $\Delta H^0_f$ = +1471 kJ kg$^{-1}$; (iii) nitroglycerol (**L5**) with α = 1.06 and $\Delta H^0_f$ = -1632 kJ kg$^{-1}$; (iv) 3,4-bis(nitroxymethyl)furazan (**L7**) with α = 0.7 and $\Delta H^0_f$ = +216.7 kJ kg$^{-1}$.
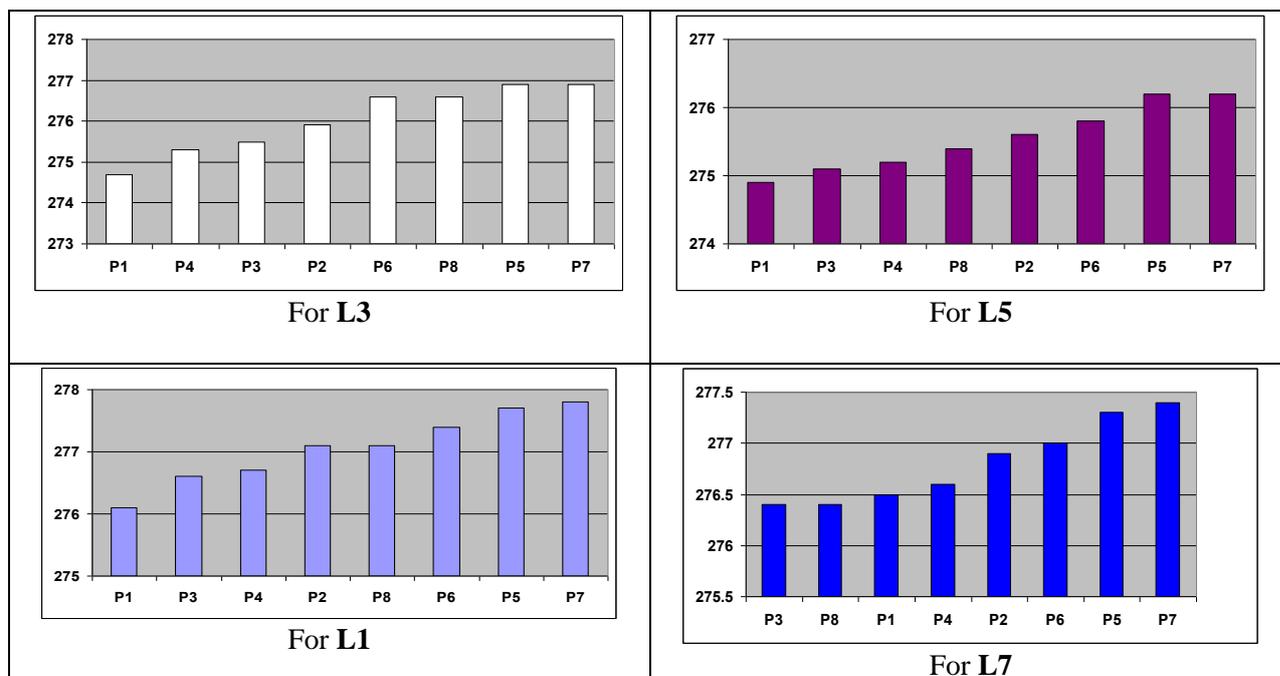
**Figure S3** Achieved values of $I_{ef}(3)$ of model SCP using plasticizers **L1**, **L3**, **L5** and **L7** in combination with 8 polymers.

From a comparison of four diagrams in Figure S3, it can be seen that, although the rank of polymers is basically the same for model SCP with all studied plasticizers, deviations are possible for plasticizers rich in active oxygen. Thus, polymer **P8** (PVMT) in model SCP with plasticizers having high α, such as **L3** or **L1**, is only slightly inferior to the leading polymers **P5** and **P7**. On the other hand, when paired with the plasticizer **L7** (α = 0.7), the propellant with polymer **P8** is already one of the worst; the lack of oxygen affects here. It should be noted that with all the polymers of this study, plasticizer **L7** with α equal to only 0.7 and not very high enthalpy of formation is only slightly inferior to **L1**. This is the result of the fact that there is no hydrogen in **L1**, and about 2% in **L7**.

When comparing 3,4-dinitrofurazan (**L1**) with nitroglycerol (**L5**), which was actually used in a typical SCP as a plasticizer,[S22] it can be seen that **L1** provides a gain of ~1.2 s in the $I_{sp}$ and $I_{ef}(3)$ values. The reason for such a gain in model SCP with **L1** is due to the significantly higher enthalpy of formation. The positive contribution of $\Delta H^0_f$ has a stronger effect on the growth of $I_{ef}(3)$ than the negative impact of the absence of hydrogen in **L1**. The comparative relative efficiency of plasticizers with each other can be easily estimated quantitatively, albeit with a certain error, using average values of coefficients $k_i$ (equation 1).

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