

Investigation towards the optimum of power capability, ageing stability and costs effectiveness on thick film resistor pastes for AlN ceramics

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Abstract

The focus of this work was the optimization of a $10 \Omega/\square$ thick film resistor (TFR) paste composition to obtain increased power capability, aging stability and minimum use of ruthenium oxide for cost savings without changing the defined narrow sheet resistance ($R_{\square}$) and temperature coefficient of resistance (TCR) specifications. In times of highly fluctuating precious metal costs, the use of a minimum of the precious metal ruthenium respectively ruthenium dioxide is one essential part for cost-effectiveness. The thick film paste formulation consists of the electrically conducting phase ruthenium dioxide, a lead-free glass phase and two inorganic additives for tuning thermo-mechanical and electrical properties of the formed films. A phthalate free organic vehicle with ethyl cellulose polymer was used to formulate a screen printable ceramic thick film paste.

For this paper, RuO_2 powders with various specific surface area values (BET) were prepared by thermal annealing of a precipitated fine ruthenium dioxide powder. All other solid and liquid components of the paste were the same as used for IKTS $10 \Omega/\square$ TFR paste FK9611 for AlN substrates. Furthermore, the content of ruthenium dioxide in the paste compositions was changed systematically around an assumed target content to achieve the desired sheet resistivity. Concurrent to the variation of the ruthenium dioxide content the inorganic additives had to be adapted too. The influence of the variations of raw material and paste composition on the film properties were investigated by screen printing 24 resistors of 2 mm x 1 mm dimension on an 1" x 1" AlN substrate, firing at 850 °C for 10 minutes in air atmosphere and subsequently measuring $R_{\square}$, TCR, the stability of resistance $\Delta R/R_0$ effected by artificial aging of the resistors (stored 100 up to 1000 hours @ 200°C) and the maximum rated power dissipation (MRPD) as well as short term overload voltage (STOL). The results are discussed in regard to find an optimum between all demands of the most important electrical film properties.

Key words

Aluminum nitride (AlN), power electronics, thick film resistor paste

I. INTRODUCTION

Aluminum nitride (AlN) with excellent heat conductivity of 170 ... 230 W/m-K is well established for power electronic applications [1], [2] due to the best compromise between heat conductivity and mechanical bending strength of the substrate. Thick film resistor (TFR) pastes on AlN ceramics are state of the art since the late nineties respectively early noughties [3]. The films were designed to withstand higher

power loads at lower temperatures compared to those deposited on Alumina substrates. One commercial disadvantage of AlN is the price, it is four to ten times higher than Alumina. Furthermore, there is a restriction to print a minimum film thickness of Ruthenium dioxide (RuO_2) TFRs especially on AlN ceramics, described in [4].

For Alumina, previous works were published showing the influence of the RuO_2 properties grain size / BET surface to the properties of TFRs like in [5]. For TFR on AlN ceramics, the results of these investigations are presented in this paper.

II. EXPERIMENTAL PROCEDURES

Powder preparation

Chemically precipitated RuO₂ powder of Heraeus Deutschland GmbH was used as raw material for preparation of RuO₂ powders of various specific surface areas (BET). The adjustment of these were achieved by annealing the material at temperatures above 500 °C for varying time in an electrical heated furnace (Carbolite Gero GmbH & Co. KG). The BET values were measured with Gemini 2390 devices of Micromeritics by flushing the samples for 2 hours at 150 °C with nitrogen before measuring in pressure ratios of p/p_0 between 0.05 and 0.20 in nitrogen. To enhance the accuracy, a filler rod was used in the balance tube of the device. To meet exact BET values, the powders were tempered while the BET-values were measured. Due to that the results varied more than 0.1 m²/g from target, blends of RuO₂ powders with specific surfaces close to target value were mixed in a dry tumbling shaker mixer (Willy A. Bachofen AG). The blend ratio was calculated with a linear blending curve between the two blending partners.

The boron oxide glass phase was prepared at temperatures above 1000 °C in a customized induction furnace with a Pt-crucible of JSJ Jodeit GmbH. The molten glass was fritted in water and dried at 150 °C in a conveyor furnace. Crushing of the frit took place in a jaw crusher of Retsch GmbH sizing the maximum glass powder grain size below $d_{\max} < 400 \mu\text{m}$. In a second milling step, a planetary ball mill Pulverisette 5 (Fritsch) was used to grind the glass down to approximately $d_{50} = 2.5 \mu\text{m}$.

Two inorganic additives (IA1 and IA2) were used for adjusting film properties like the temperature coefficient of the resistance of the TFR and physical film formation. Their powder properties were tuned with aforementioned equipment.

The organic vehicle was prepared by dissolving an ethyl cellulose polymer in terpineol at a temperature above 60 °C in a stirred and electrically heated round bottom flask.

Paste formulation

Table 1 illustrates, that three pastes were prepared and tested from each RuO₂ powder using 36, 39 and 42 percent by volume in the TFRs. This RuO₂ volume concentration range was estimated from 10 Ω/□ TFR compositions described in literature. The inorganics content was adjusted in a certain defined ratio to complement 100%.

Table 1: the paste's solids compositions in Vol%

V (RuO ₂)	V (Glass)	V (IA 1)	V (IA 2)
36	46	In sum 18	
39	46	In sum 15	
42	46	In sum 12	

Table 2 shows paste compositions and specific surfaces of the investigated resistor pastes.

Table 2: Paste composition (volume concentration V_{RuO2}) and RuO₂ powder specific surface (BET).

Paste	BET [m ² /g]	V _{RuO2} [Vol%]
A1	12	36
A2	12	39
A3	12	42
B1	15	36
B2	15	39
B3	15	42
C1	16	36
C2	16	39
C3	16	42
D1	18	36
D2	18	39
D3	18	42
E1	19	36
E2	19	39
E3	19	42
F1	22	36
F2	22	39
F3	22	42

The required powders were weighed in and mixed dry in a ball mill. The powder mixture was agitated into the organic vehicle in a mortar mill of Retsch GmbH as a first dispersion step. The final dispersion was achieved by processing the paste on a three roll mill EXAKT 120E (EXAKT Advanced Technologies GmbH). With a solids content of 72 wt%, smooth, easily screen printable thick film pastes were obtained.

Sample preparation and test methods

Samples for electrical testing of the TFR were prepared using a layout containing 24 single resistors sized two by one millimeters length by width to secure a certain statistical confidence level. The IKTS test layout is shown in Figure 1, with metallization in green and resistors in red. For printing the metallization pads, of the IKTS AgPd conductor paste for AlN FK1205 was used.

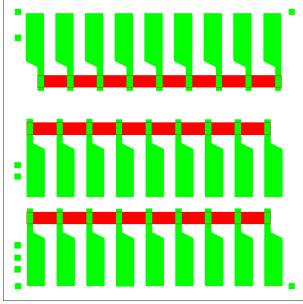


Figure 1: IKTS test layout.

The pastes were screen printed using an EKRA Microtronic II printing machine (200 mesh size steel screen, 40 μm wire diameter, 25 μm emulsion with 5 to 10 μm emulsion over mesh) on 1" x 1" AlN substrates AN180 (CoorsTek). The wet films were levelled at room temperature for 10 Minutes, dried for 15 minutes at 150 $^{\circ}\text{C}$ and fired at 850 $^{\circ}\text{C}$ in an air atmosphere belt furnace with a dwell of 10 minutes and total cycle time of 60 minutes (Fig. 2).

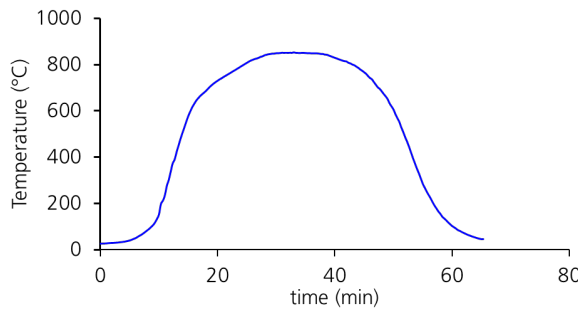


Figure 2: firing profile with 60 minutes cycle time.

All film thicknesses were measured with an auto focusing laser scanning profilometer AF16 of OPM Messtechnik GmbH for accurate and fast thickness measurements.

Resistance R_{30} was measured with a four wire probe method at 30 $^{\circ}\text{C}$ for precise results. From all 24 resistors an arithmetic average value was calculated for each substrate. The sheet resistivity R_{Sq} was calculated and normalized to a standard dried film thickness of 22 μm according to (1).

$$R_{Sq} = \frac{R_{30}}{Sq} \cdot \frac{MDTR}{22 \mu\text{m}} \quad (1)$$

where Sq is the number of squares in the layout and $MDTR$ is the mean dried film thickness of the resistor.

The temperature coefficient of the resistance (TCR) was obtained by measuring the resistors at varying temperatures between -55 and 150 $^{\circ}\text{C}$. The TCR itself is defined by

$$TCR = \frac{R_T - R_{25}}{R_{25}} \cdot \frac{1}{T - 25^{\circ}\text{C}} \cdot 10^{-6} \quad (2)$$

with R_{25} as resistance at reference temperature 25 $^{\circ}\text{C}$ and R_T as resistance at temperature T .

For better comparison of different results each curve was fitted by method of least squares and the so-called hot- and cold-TCR (HTCR, CTR) were calculated from R_{150} and R_{-55} respectively $T=150^{\circ}\text{C}$ and $T=-55^{\circ}\text{C}$.

To measure the aging stability against humidity, the resistors were stored in a Vötsch VC0018 climate chamber at a temperature of 85 $^{\circ}\text{C}$ and 85% relative humidity. The initial resistances of each resistor were measured after firing and following after $t=100, 250, 500$ and 1000 hours storage. The drift of the sheet resistances was calculated according to (3).

$$\frac{\Delta R_t}{R_0} = \frac{R_t - R_0}{R_0} \quad (3)$$

TFR-stability against power pulses was measured using the STOL method (STOL= Short Term Overload Voltage). STOL measurements consists of the initial resistance measurement at room temperature ($R_{0,cold}$) and an addition caused by step-by-step increasing power pulses. One power pulse or electrical load is applied for 5 seconds. At the end of this pulse the resistance R_{hot} and temperature T_{hot} are measured. Then a 60 seconds break is following for cooling the substrate to room temperature. At the end of the break the resistance R_{cold} and T_{cold} are measured before applying another pulse. With every load pulse the power was increased by 5 Watts. The main principle of the measurement is also shown in Figure 2.

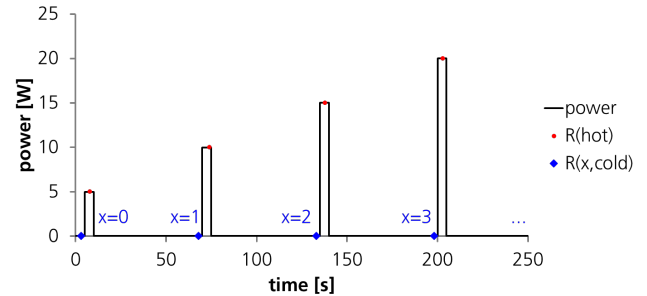


Figure 3: STOL measurement principle.

STOL voltage U_{STOL} is reached when the shift of resistance $\Delta R_{x,cold}/R_{0,cold}$ exceeds 0.1%. From these measurements the parameter maximum rated power dissipation (MRPD) was calculated according to (4).

$$MRPD = \frac{(0.4 \cdot U_{STOL})^2}{R_{Sq}} \quad (4)$$

III. RESULTS

The most important electrical film properties of the pastes which were examined are shown in the following Table 4.

Table 3: composition details of pastes and corresponding electrical film properties

Paste	R_{sq} [Ω/sq]	HTCR [$10^{-6}/K$]	CTCR [$10^{-6}/K$]	$\Delta R_{100}/R_0$ [%]	MRPD [W/mm ²]
A1	19,3	21	-51	0,12	3,3
A2	13,6	70	1	0,07	4,8
A3	11,5	156	114	0,02	4,7
B1	15,2	62	-10	0,14	4,1
B2	11,9	96	29	0,06	4,4
B3	8,7	125	65	0,02	5,7
C1	13,7	57	-18	0,10	3,7
C2	10,4	86	17	0,08	4,3
C3	8,1	116	49	0,04	4,6
D1	12,3	40	-39	0,30	4,4
D2	9,6	68	-6	0,05	4,3
D3	8,4	99	33	0,05	3,9
E1	12,2	44	-33	0,35	2,9
E2	9,6	72	-2	0,09	4,3
E3	7,1	89	17	0,05	4,2
F1	9,8	5	-79	0,44	3,6
F2	7,7	31	-49	0,51	3,8
F3	5,8	49	-30	0,14	4,3

To illustrate the results and its dependencies in detail, the following charts of Fig. 4 to Fig. 7 are drawn.

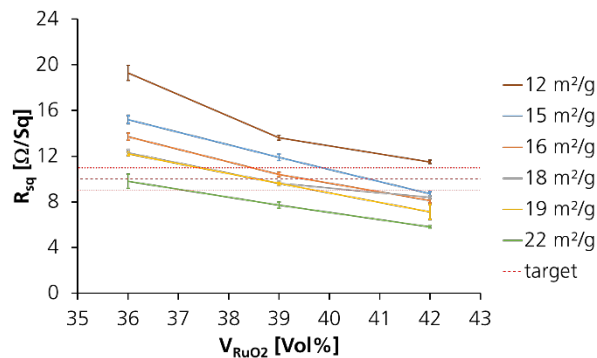


Figure 4: sheet resistivity normalized to 22 μm dried film thickness in dependence of V_{RuO_2}

Figure 4 shows that the mean values of sheet resistivity are decreasing systematically with increasing volume of conductive phase in a linear relationship. The lower the BET value of – respectively the coarser – the used RuO_2 powder is, the higher the sheet resistivity gets compared to the results of the pastes with the same volume of conductive phase.

Taking the corresponding hot-TCR into account, Fig. 5 likewise reveals a linear relationship between the HTCR results and sheet resistivity R_{sq} . The results of the pastes with RuO_2 powder of 12 m^2/g at ca. 14 Ω/sq and 20 Ω/sq seem to deviate from that behavior showing lower HTCRs than expected and the deviation of both parameters is significantly higher than for any other paste composition. Thus, these two results are not considered for discussion.

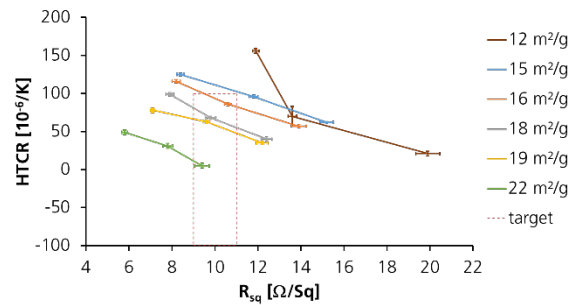


Figure 5: Hot-TCR in dependence of R_{sq} and BET surface

The results of the CTCR measurements are comparable to the general behavior of the HTCR, only the absolute values are approximately 50...70 $\cdot 10^{-6}/K$ lower than the corresponding HTCR's. Hence, insertion of another plot showing the same was avoided.

Figure 6 depicts the aging values $\Delta R_{100}/R_0$ of the resistors after 100 hours. All values are smaller than 1 %, most values are below 0.1%. There is one hint for a tendency visible which appears to be a combination of the two impacts: the finer the used RuO_2 powders and the smaller the volume fraction RuO_2 in the solids composition, the higher the resistivity change exhibits. This assumption is strengthened when looking at the relative resistance changes after 1000 hours in Fig. 7. The numerical results for this diagram are not listed in Table 4 due to lack of space but the illustration of these values demonstrate even more than the pure numbers.

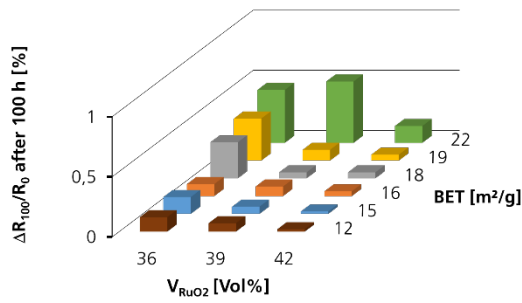


Figure 6: Artificial aging in relative humidity after 100 h in dependence of V_{RuO_2} and BET surface

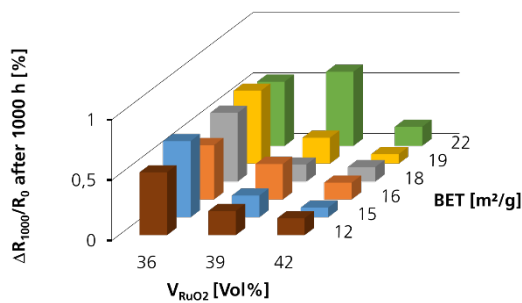


Figure 7: Artificial aging in relative humidity after 1000 h in dependence of V_{RuO_2} and BET surface

The results of power load measurement are visualized in Fig. 8 and Fig. 9. In general, the voltage U_{STOL} is slightly decreasing with increasing volume fraction of RuO_2 and accordingly, no major influence neither of volume fraction RuO_2 in the film nor of fineness of used RuO_2 powder can be clearly stated for maximum rated power dissipation.

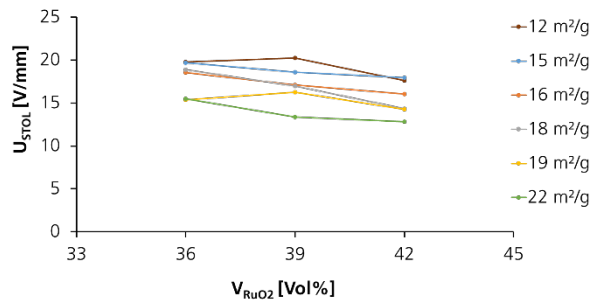


Figure 8: U_{STOL} in dependence of V_{RuO_2} and BET surface

As restriction for the Figures 8 and 9 it has to be noted that as the STOL measurements were not completed for every of the 24 resistors of each substrate, only the one resistor in the center of the substrate was taken for this assessment and thus there is no statistical validation possible yet for these results.

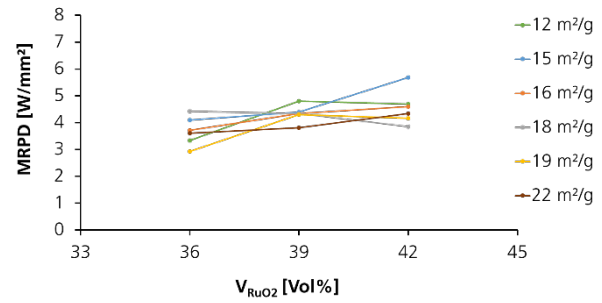


Figure 9: MRPD in dependence of V_{RuO_2} and BET surface

IV. DISCUSSION

The results show in general that with the obtained RuO_2 powder properties several constellations for paste compositions are possible to achieve a $10 \Omega/\square$ TFR paste from the sole point of view of sheet resistivity. Figure 4 depicts the physical dependency of the sheet resistivity from volume fraction of RuO_2 and its BET values and the target sheet resistivity $10 \Omega/\square \pm 10\%$. It corresponds to the theoretical behavior that with increasing amount of Ruthenium dioxide the resistance decreases. Depending on the BET value of the used RuO_2 powder, the needed volume fraction of RuO_2 varies from about 41 ... 36 Vol%. The finer the Ruthenium dioxide can be dispersed among the glass phase, the smaller is the distance between conductive particles along the percolation paths and thus the lower the resistivity exhibits. Disregarding all other film parameters, the RuO_2 powder with 22 m^2/g BET would be best for achieving a $10 \Omega/\square$ paste while saving the most precious metal content respectively costs because only 36 Vol% RuO_2 would be needed.

Involving the results for the HTCR to the consideration, it is necessary to use a volume fraction of RuO_2 of 39 Vol% to stay within target range, except if the finest powder is used. Then, the composition can be lowered down to 36 Vol% RuO_2 (green lower left dot in Fig. 5). The reason for the effect - that the finer BETs are the lower the TCR occurs - is that with rising BET the grain size is reduced. So the mean path of the electron consists of more grain borders RuO_2 / glass and thus the ratio of electronic conduction to semiconducting effects is lowered. This assumption is only valid if the grain size change of RuO_2 is small against the grain size ratio of RuO_2 and glass so that the general distribution of the phases in the film is not changed drastically.

The results of artificial aging in Figure 6 show very high stabilities. The most resistance changes are near the detection limit of 0.02%. The worst result of change is closest to $\Delta R_{100}/R_0 \leq 0.5\%$ for the pastes F1 and F2. Nevertheless, in combination with the results of Pastes D1 and E1 one could assume that the finer the used RuO_2 powders are and the smaller the volume fraction RuO_2 in the solids composition

is, the higher the resistivity change exhibits. So with rising BET values, the aging stability gets slightly worse. This trend is emphasized when adding the information given in Fig. 7. After 1000 hours of artificial aging it is clearly visible that not only the “high BET resistors” drift but all the pastes A1, B1, ... F1 with 36 Vol% RuO₂ content are at a level of about 0.5% and thus comparably higher than the ones of pastes A2 to F2 and B3 to F3 respectively with 39 and 42 Vol% RuO₂. Except for paste series F with the highest BET value, there is also a trend visible that the higher the RuO₂ content is, the more stable the resistors are.

One general explanation for the changes in resistance can be that the TFR on AlN exhibit a designed porosity because RuO₂ and AlN can react while firing, forming nitrogen gas. [4] Any chemical reaction – probably a reaction with water of the humidity of the aging atmosphere – can have an influence on the molar volume of the ruthenium phase and the specific resistivity can be changed. Thus, the electron conducting paths are slightly changed. Distances between electrically conducting grains can increase, the resistance rises. The precise mechanism behind the resistivity change specifically of these TFR’s was not examined within this study.

Additionally, with high BET surfaces respectively with low grain sizes of RuO₂ there is an increased activity of the particles and thus their interaction with the environment can take place faster. This is why after only 100 hours aging, the change in resistance of paste series F1-F3, D1, E1 and may be E2 is higher than the rest. After 1000 hours aging, the change of resistance affects more paste formulations. The pastes A1 to D1 with 36 Vol% caught up with its composition-congeners with high BET values (E1, F1), but the pastes with higher volume fractions of RuO₂ still show low resistance increases after artificial aging. But the degree of the aging within one paste series (within A1 to A3 or within B1 to B3 etc.) should be exactly the same due to the same specific surface and chemical composition. So why are there still differences measured in resistance changes? The explanation for this can be found in the microstructure of the film. Within a paste series with the same letter, the content of RuO₂ rises with the rising number but the BET / grain size of RuO₂ is held constant. Thus, films of the pastes with numbers 1 have less percolation paths of the conducting phase and subsequently the influence of a change of the molar volume of the conducting phase caused by any chemical reaction is higher. Hence, the change of resistance is measurably higher than in films of pastes with higher numbers.

Pleasantly, all results of artificial aging are lower than 1%, as they should be according to the specification, so there is no limiting factor for the final application as 10 Ohm/□ resistor paste FK9611 of IKTS paste system FK9600. To get the best results for matching R_{Sq} and HPCR as well as lowest

possible aging stability, the paste should be composed from a RuO₂ powder between 18 or 19 m²/g BET and with a content of 39 Vol% RuO₂. For cost-effectiveness, may be a composition in between 36 and 39 Vol% would be better.

Concerning the power capability drawn in Figure 8, no major influence of the BET value can be derived. The results vary roughly around a plateau of about 4 W/mm². Since the STOL-Voltage is decreasing with rising content of RuO₂ and with this, the resistance is lowered, it is consequential that the maximum rated power dissipation stays on a same level because of (4). But as restricted before, due to lack of statistical data only an approximate conclusion of the results is possible.

V. CONCLUSION

It was shown that specific surface of the RuO₂ powder has an influence on the electrical properties of RuO₂ thick film resistors. The way to design the paste respectively film composition depends on which target values have to be achieved. There is the need to match criteria for R_□, TCR, aging stability and power capability among others.

Besides aforementioned technical properties, there is a pure economic need for optimization of the composition. The difference in commercial value of a RuO₂ TFR paste with a content of 36 Vol% or 42 Vol% conductive phase is about 6 to 10%, regarding the current precious metal price of Ruthenium rising from one high to the next in 2018.

The present work enables IKTS to adjust the 10 Ω/□ RuO₂ TFR paste to an optimum between technical demands and commercial needs. The author recommends the usage of a Ruthenium powder of 18 or 19 m²/g with a paste composition of 37.5 to 39 Vol% as an optimum of all investigated parameters and including price issues. Furthermore, the results obtained demonstrate that for example a development of a new high precise resistor paste system with narrow TCR ≤ 30·10⁻⁶/K specification is conceivable.

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