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Tailoring the nonlinear conducting behavior of silicone composites by ZnO microvaristor fillers

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ABSTRACT: Silicone composite filled with zinc oxide microvaristors possesses excellent nonlinear conducting behavior as ZnO varistor does. For better adjusting the composite's electrical behavior to satisfy the practical field-grading requirement, this article studied the influence of ZnO filler's property on the nonlinearity of the composite. Several groups of ZnO-silicone composite samples in different filler volume fraction and filler diameter were prepared, the measured *J-E* characteristics show that the percolation threshold of ZnO-silicone composite is around 35%, above which the composites present reliable nonlinear behavior. The switching voltage of the composite exhibits a considerable decrease as filler's diameter increases or filler's volume fraction increases, while the nonlinear coefficient remains stable. Moreover, filler's size also has a little influence on composite's percolation limit. The conclusion above fits very well with the theory of the conducting composites and percolation process. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42645.

KEYWORDS: composites; conducting polymers; dielectric properties

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INTRODUCTION

Polymer blended with microvaristor fillers can function as field grading material (FGM) due to its excellent nonlinear *J-E* characteristics. It possesses field-dependent electrical parameters thus is widely used in high voltage applications for stress control. Many researches have been devoted to polymeric composites based on ZnO varistor fillers for the purpose of field grading. It is reported that ZnO-silicone,[1] ZnO-epoxy,[2] ZnO-LDPE[3] composites exhibit desirable nonlinear conducting behavior when the filler volume fraction exceeds a certain value, namely the percolation threshold. Particularly, ZnO microvaristor filled silicone rubber composites is with great potential in high voltage insulation system. They can be applied in outdoor insulators to tune the seriously non-uniform voltage distribution caused by the stray capacity between the insulator and the pole structure.[4] Moreover, ZnO-silicone composite also perform FGM functions in HVDC cable system.[5] In prefabricated cable joints a continuous FGM layer can be designed to cover the inner deflector or the metallic connector part for stress grading while in the cable termination the FGM layer is combined with a stress relief cone to connect the ground and the live electrode.

Theories have been developed for the application of FGM[6] and through numerical calculation and simulation the optimal FGM parameters can be determined.[7,8] Two important parameters are the switching field E_b and the nonlinear coefficient α. The value of α is expected to exceed 10, above which the enhancement of α makes little difference[6] while E_b is designed according to specific field grading case. Thus the main task is to tailor the ZnO-silicone composites' conducting behavior to meet the requirement of FGM parameters. A flexible control of the *J-E* characteristics can be realized by adjusting the composite's basic physical property, like filler concentration and diameter range, which is easy to modulate.

Researches have been undertaken into the nonlinearity of ZnO-LLDPE[9] and ZnO-epoxy[2]composites with different filler volume fraction and meanwhile the percolation limit is also determined. However, the effect of fillers' diameter to the nonlinear behavior of the composites has been absent in relevant study.

This article investigated the nonlinear conducting behavior of ZnO-silicone composite with various filler's diameters and volume fractions and concluded how these filler's property influences the nonlinear characteristics of the composite. Moreover, the theory of conducting composites and percolation process is applied to explain the measurement results.

EXPERIMENTAL

Preparation of ZnO Fillers

In order to acquire ZnO fillers with better unity and electrical property, the formulation and sintering technique of ZnO varistor discs with different properties were introduced[10–16] into the preparation of ZnO microspherical varistors, which were based on the conventional formula as 95 mol % ZnO + 1.0 mol %

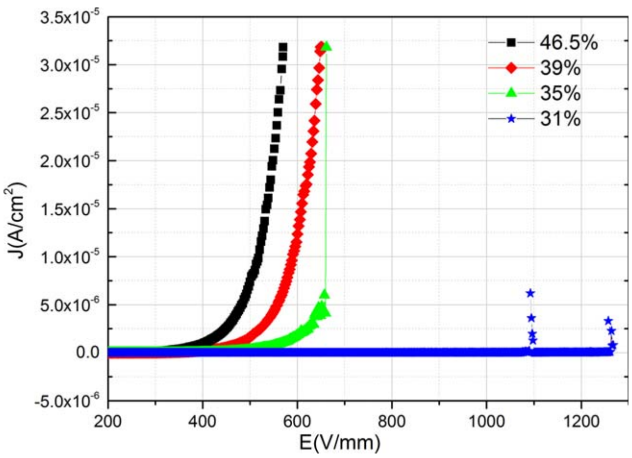

Figure 1. The nonlinear *J-E* characteristics of ZnO composites with filler's diameter ranging in 100–125 μm in particle volume concentrations of 46.5%, 39%, 35%, and 31%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Bi_2O_3 + 0.5 mol % MnO_2 + 1.0 mol % Co_2O_3 + 0.4 mol % Cr_2O_3 + 1 mol % Sb_2O_3 + 1.0 mol % SiO_2 + 0.1 mol % Al_2O_3. The mixed powder was sent into ball mill and blended in anhydrous alcohol for 8 h. After addition of organic binder, the aqueous slurry was processed by the spray-dried machine and the mixture was granulated into spherical particles, which basically determined the size of microvaristors. Hereafter, the microspheres were sifted and then sintered at the temperature of 1200°C for 4.5 h with the heating rate of 0.55°C/min and cooling rate of 1.6°C/min. After disagglomeration and sieving, the size of manufactured microspheres ranged from 50 to 150 μm.

Preparation of ZnO-Silicone Composite

ZnO microvaristor composites based on silicone matrix were then prepared. The silicone and vulcanizing agent were mixed in 0.8 wt % with tetrahydrofuran solvent and blended by a high torque blender for about 20 min. After silicone was fully dissolved in the solvent, ZnO microvaristor powders were poured into the liquor and the blending continued for 40 min. Then the mixture was dried in a vacuum oven for more than 10 h till the solvents fully volatilized. After that was the process of vulcanization. Each time 3 g of mixture was pressed by the vulcanizing machine in the pressure of 15 MPa at 170°C for 15 min and then naturally cooled to room temperature in the same pressure. The acquired silicone composite sample is about 0.5 mm in thickness and 20 mm in diameter.

Sample Grouping and Measurement

ZnO fillers were sieved into four groups with diameter in the range of 50–75 μm, 75–100 μm, 100–125 μm, 125–150 μm, respectively. Then four groups of fillers were mixed into silicone matrix according to four volume fractions, 31%, 35%, 39%, 46.5%, respectively. So that 16 groups of ZnO-silicone composites samples in different filler diameter range and filler volume fraction were prepared. After the deposition of golden electrode onto the surfaces of composites sample, the $I(U)$ measurement was simply performed by power source (Kiethley2410C). The $J(E)$ characteristic of the samples are acquired from the measured I-U curve by eqs. (1) and (2):

$$J = I/S \tag{1}$$

$$E = U/d \tag{2}$$

where d and S are the thickness and cross-section of the sample.

RESULTS AND DISCUSSION

The Effect of Filler Concentration to the Composite's Nonlinear Behavior

Nonlinear *J-E* curves of ZnO composites with filler's diameter range of 100–125 μm in different particle concentrations, 31%, 35%, 39%, 46.5% are shown in Figure 1. Samples with other filler diameter ranges exhibit similar pattern that vary with filler's concentration.

Figure 1 shows that as the filler concentration increases, the arising of nonlinearity comes earlier, which means a lower switching field. The 46.5% vol and the 39% vol case both present typical nonlinear properties and the two curves are near in parallel, which means similar nonlinear coefficient. In the 35% case, as the electric field increases the nonlinear *J-E* feature first begins to arise. But the current density J suddenly jumps to the upper limit as soon as exceeding 5 μA/cm^2. Subsequently, repeated measurement of the same sample in next few hours shows standard nonlinear *J-E* curves with much lower switching voltage, as shown in Figure 2. However, few days later, the same sample is measured once more and exhibits almost identical feature as the first time measured curve shows. When it turns to samples in 31% vol, they fail to present nonlinear behavior. The current density shows slight increase only in relative high electric field but soon falls to low level as E increases.

Figure 3 is the schematic diagram of fillers distribution as well as conduction path in ZnO microvaristor composites, which may explain the mechanism of composites' nonlinear property varying with filler's concentration. In samples with relative high

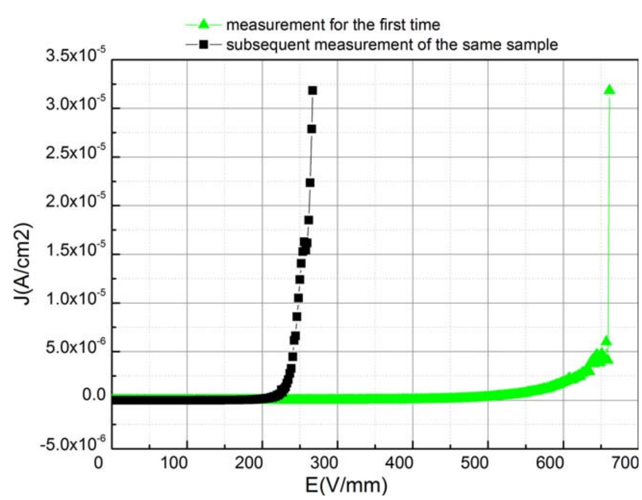

Figure 2. *J-E* characteristics of the same ZnO composite samples with filler range of 100–125 μm in 35% vol in repeated measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

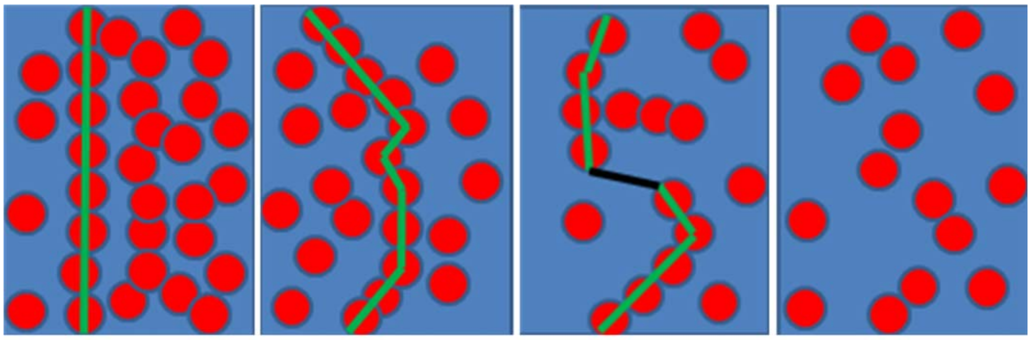

Figure 3. The schematic diagram of the filler distribution and conduction path in ZnO-microvaristor composites with different filler concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

filler concentration, like the 46.5% vol case, several conduction paths coexist and the current is likely to choose the shortest path to pass through, shown as Figure 3(a), the green line represents the possible conduction path. Whereas in samples with lower concentration, like the 39% vol case, fewer conduction paths exist and the path may be roundabout, as shown in Figure 3(b). Moreover, lower filler concentration means less compact contact between fillers, which leads to a higher contact resistance.[17] Thus as filler concentration decreases, the switching field is higher due that less conduction paths exit and the resistance of a single path increases. When filler's volume fraction is further reduced like the 35% vol samples, in the whole composite there is no thorough conduction path and the most potential path is just blocked by a small gap of silicone, shown as Figure 3(c), the black line represents the silicone gap. When a step voltage is applied on the sample of Figure 3(c) case, current may increase but is limited due to the restrict of the silicone gap. When the electric field is high enough, fillers in the potential path(the green line) exhibit nonlinear property thus undertakes quite low voltage. As a result, the small silicone gap(the black line) sustain most of the applied voltage and break through immediately due to a very high field. Thus the measured current suddenly jumped to the upper limit as the 35% sample showed in Figure 1. When repeated measurement is conducted on the same sample, the breakthrough silicone gap can be regarded as a conducting path hence a considerably shortened conduction path is formed in the composites. Under the circumstance, the sample exhibits a typical nonlinear characteristics. However, several hours later the silicone gap can recover due to its fluidity and presents similar *J-E* pattern as the first measurement presents. Finally in the 31% samples, shown as Figure 3(d), an even lower filler concentration leads to enough silicone gaps to block a thorough conduction path. Thus when high voltage is applied the current present an occasionally increase but fail to exhibit a stable nonlinear characteristics.

Moreover, in samples with 35% vol samples, ZnO fillers can form a nearly thorough conduction path which is impeded only by very thin silicone gaps. And when filler concentration is little higher than 35%, the composites possess stable nonlinear *J-E* property, as samples with 39% vol fillers do. This indicates that the percolation threshold of the ZnO-silicone composite with filler diameter range of 100–125 μm is 35%, above which the composites begin to exhibit field–dependent conducting behavior.

ZnO microvaristor filled related polymers, like ZnO-epoxy,[2] ZnO-LDPE,[3] ZnO-LLDPE,[9] ZnO-polyester[18] are reported to possess different nonlinear characteristics with switching fielding in the range of about 300–1000 V/mm and nonlinearity above 9. The difference is mainly due to the nature of the grain parameter like grain size and preparing formula inside each microvaristor.

Even so, all of above ZnO composites present similar pattern that the nonlinear conducting behavior vary with filler concentration. The switching field decreases with the incremental filler concentration above the percolation threshold while the nonlinear coefficient remaining stable. And under the threshold, the composites can hardly exhibit nonlinearity. The case of local polymer breakdown may not be observed in previous study because that requires specific filler concentration as well as many repeated measurement to verify it.

The percolation threshold of ZnO filled polymers are also in discrepancy. That of ZnO-silicone composites investigated in this article is about 35% and ZnO-polyester[11] shows similar threshold of about 40%. Also some researches indicated that in ZnO composites like ZnO-silicone,[1] ZnO-epoxy[19] a high filler concentration of typically 40% vol is required to obtain nonlinear electrical conductivity. However, In the case of ZnO-epoxy,[2] ZnO-LDPE,[3] ZnO-LLDPE[9] the percolation threshold are reported to be 20%, 20%, and 25%, respectively. The measured low percolation threshold may be due to a nonuniform dispersion of the fillers in the insulation matrix because conduction path is easier to form when fillers gather together and then the composites can exhibit nonlinearity more early. Thus measured thresholds in the range of 30%–40% vol is more reliable than 20%–25% ones. Nonlinear composites with other fillers also features as relative high percolation threshold, like polyaniline emeraldine base and carbon black filled EPDM[20] are in threshold of near 30% and that of SiC-EPDM composites with rounded SiC fillers are 33%,[21] which are quite close to the 35% threshold determined in this article.

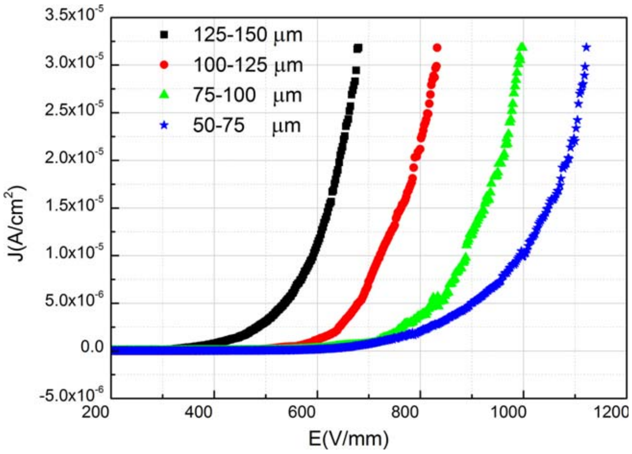

Figure 4. Nonlinear $J(E)$ characteristics of ZnO composites in particle concentrations of 39% vol with filler's diameter range of 50–75, 75–100, 100–125, 125–150 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Effect of Filler Diameter to the Composite's Nonlinear Behavior

The *J-E* characteristics of 39% ZnO-silicone composites samples with filler diameter in the range of 50–75, 75–100, 100–125, 125–150 μm, respectively, are shown in Figure 4. The switching field E_b and the nonlinear coefficient α of the samples with various filler diameter range in the filler volume fraction of 46.5% and 39% are listed in Table I, in which α and E_b are the average value of more than five samples in the same prepared sample group. The nonlinear coefficient α is defined by eq. (3).

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} \tag{3}$$

where $J_2 = 30$ μA/cm^2, $J_1 = 3$ μA/cm^2, E_2 and E_1 are corresponding electric field of J_2 and J_1 according to the measured *J-E* curve of the sample, and E_1 is defined as the switching field E_b. Most of samples in 35% and 31% filler concentration, except those with filler diameter range of 125–150 μm, either present sudden current uprush due to local silicone breakthrough like 35% case in Figure 1 or fail to exhibit stable nonlinear behavior, thus their switching voltage and nonlinear coefficient are not counted and listed.

From Figure 4 and Table I we can see that in 39% ZnO composites, as the filler's diameter increase the composites' switching field decrease while the nonlinear coefficient is almost identical. The *J-E* curves in Figure 4 are almost parallel, which indicates very similar nonlinear behavior except the switching field. In other word, the increase of filler's diameter leads to the translation of the composite's *J-E* curve toward negative direction along the E axis. This offers a good approach to adjust the composites' switching field. In 46.5% vol samples, as filler diameter increases the switching voltage become much lower as well and the nonlinear coefficient shows considerable increase.

The mechanism of the effect of filler diameter range can be explained by the theory of conduction composites.[22] As discussed in "The Effect of Filler Concentration to the Composite's Nonlinear Behavior" section, the contact resistance between ZnO fillers also contributes to the overall switching voltage of the composites. In the same filler volume fraction, greater filler diameter means fewer fillers in the composites, thus contact interface between fillers is also less. In addition, bigger filler size leads to a greater contact area, which decreases the contact resistance.[23] Thus in the composites with greater filler diameter, there are few contact interface in conduction path and each interface possesses lower contact resistance. Under the circumstance, the total contact resistance of the composites can be much smaller and the higher voltage is applied on the filler itself. Therefore, fillers will sooner present nonlinear behavior and the switching field of the composite is decreased. That is the reason why composites with greater filler diameter presents lower switching field.

As for the nonlinear coefficient α, in composites with relative lower concentration like 35% vol samples, only few conduction paths are active when high voltage is applied. Thus the nonlinearity of the composites only depends on the property of the interior grain boundary inside each particle, which is determined by the manufacturing process. As all blended ZnO fillers are prepared in the same batch and are in relative well unity, the composites present a stable nonlinearity which is almost independent with the filler's diameter. In composites with high filler concentration like 46.5% vol samples, more conduction path is switched on and the amount of conduction path will also contribute to the composites' nonlinearity α. In composites with greater filler, the conduction path is less likely to be roundabout and the path is easier to be switched on. In this case, more conduction path is active when high voltage is applied and the current density presents a sharper increase, which indicates a higher nonlinearity α. Thus more active conduction path result to greater α, that's why in Table I the α of 46.5% vol samples present considerable enhance when filler diameter is larger. This also explains the fact that the nonlinearity of 46.5% composites is higher than that of 39% with same filler diameter range.

Table I. Switching Field E_b and the Nonlinear Coefficient α of the 39% and 46.5% Samples with Filler's Diameter Range of 50–75, 75–100, 100–125, 125–150 μm

		Filler diameter range (μm)			
Nonlinear property	Filler concentration	50–75	75–100	100–125	125–150
E_b (V/mm)	46.5%	522.8	419.2	408.0	329.4
	39%	826.5	780.0	575.1	506.7
α	46.5%	10.2	12.6	12.7	17.5
	39%	10.2	10.3	10.0	10.8

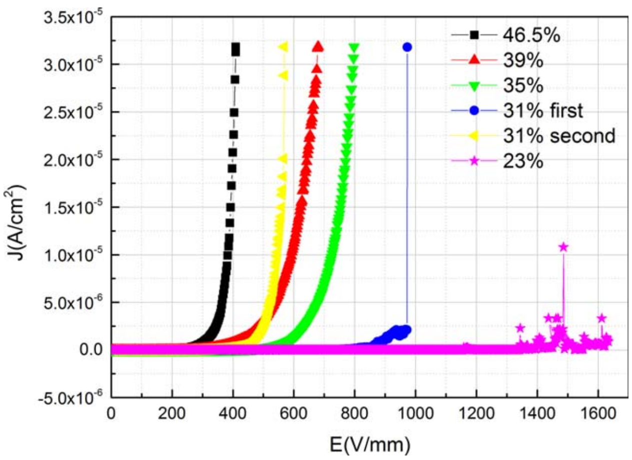

Figure 5. Nonlinear conducting characteristics of ZnO composites with filler's diameter range of 125–150 μm in particle concentrations of 46.5%, 39%, 35%, 31%, 23% vol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Filler Diameter to the Composite's Percolation Threshold

The filler diameter also has an effect on the composite's percolation threshold. The *J*(*E*) characteristics of samples with filler's diameter range of 120–150 μm in particle concentrations of 46.5%, 39%, 35%, 31%, 23% vol is shown in Figure 5. Compared with Figure 1 we can see that when filler diameter range is 125–150 μm, the 31% vol samples present local silicone breakthrough characteristics which in Figure 1 appear at 35% vol samples while in Figure 5 the sample has already exhibited stable nonlinear *J-E* pattern at the volume fraction of 35%. However, when filler diameter is in the range of 50–75 μm, which is not presented in this article for the brevity, many 35% vol samples cannot even form a conduction path as in Figure 1 31% vol samples shows and even some 39% vol samples exhibit current uprush due to silicone breakthrough. Sample's with filler range of 75–100 μm shows nearly identical *J-E* characteristics to that of Figure 1 when samples are in the same filler concentration. Above measurement results indicate that samples with greater filler diameter can exhibit nonlinear conducting behavior in an even lower concentration while ones with smaller fillers require higher filler volume fraction for the arising of nonlinearity. In other words, the increase of filler diameter can reduce the composite's percolation threshold in a small range. This summary is identical to the discussion in "The Effect of Filler Diameter to the Composite's Nonlinear Behavior" section, that in composites with greater filler diameter it is easier to form a conduction path, thus less filler volume fraction is required to reach the percolation threshold. In addition, the fillers are ellipsoid rather than regular spherical thus each particle has major axis and minor axis, the ratio of which is defined as aspect ratio. In percolation theory, more irregular fillers possess greater aspect ratio and when blended in matrix the composite presents a lower percolation threshold.[24,25] ZnO fillers with different diameter range in this article are prepared through sifting, which mainly depends on particle's major axis. Thus the sifted greater fillers have greater aspect ratio and hence the corresponding composites exhibit decreased percolation threshold. This is also a factor leading that the increasing filler diameter reduces the composites' threshold.

CONCLUSIONS

The nonlinear current-voltage behavior of ZnO microvaristor-silicone composites are influenced considerably by the filler's concentration and diameter. When filler concentration increases to the percolation threshold, which is around 35%, the composites present local silicone breakthrough featured as current uprush. In further higher concentrations, a stable nonlinear *J-E* characteristic appears and the switching field decreases while the nonlinear coefficient enhances with the increase of filler volume fraction. When filler concentration is slightly above the percolation threshold, as the filler diameter is greater the composites' switching field is decreased whereas the nonlinear coefficient remains identical. This offers great convenience to the design of field grading according to practical switching field requirement. In higher filler concentration like 46.5% vol, more active conducting paths arise thus composites exhibit decreased switching field and enhanced nonlinearity as filler diameter increases. The increase of filler diameter can also reduce the composite's percolation threshold in a small range. The summary above presents very well fit with the theory of the conducting composites and percolation process.

In addition to the points that the article has focused on, ZnO composites' nonlinear conducting behavior is also influenced by some other factors, among which the aging characteristic may play a considerable role. In the case of ZnO varistors, aging and degradation may give rise to deformation of double-Schottky barrier and deterioration in electrical property such as the leak current, and eventually result in protection failure.[26,27] In ZnO microvaristor composites, the same problem may also exist and could lead to a decreased switching field as well as degraded nonlinearity, which are quite likely to influence the composites' field grading function. Thus future work is expected to shed light on aging behavior of ZnO microvaristors composites and this is significant to their stable long-term operating as FGM.

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