Experimental Evaluation of the Curing of Unsaturated Polyester Resin at Various Amounts of Methyl Ethyl Ketone Peroxide, Cobalt Octoate and Porcelain Powder

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Abstract. *The goal of this research is to investigate the impact of the three parameters on the cure of the unsaturated polyester resin. The obtained values show the influence of each parameter on the cure and hence enables to establish a time-range with regard of the percentage of the components for a good management of the curing process.*

Keywords*: Unsaturated polyester resin, porcelain powder, gel time, exotherm temperature, curing process, X-ray diffraction.*

1.Introduction

Today, unsaturated polyester resins (UPRs) plays an important role in the industry mainly due to its low price, easier handling, as well as ease of association with reinforcement [1, 2].

The curing of this polyester backbone by the unsaturated acid constituent in combination with a vinyl component creates a three-dimensional structure [3]. Inorganic particulates as fillers are widely used in polymer compounds to improve physical properties and to reduce the final cost. In recent years, polymer composites have drawn increasing interests due to the significant improvements of material properties at very low or hight loading.

Unsaturated polyester resin curing reactions can be controllable by adjusting both the types and amount of curing agents, accelerators and inhibitors (additive agents). In general, gel and cure times are controlled by modifying the amount of these additives [4].

The curing reaction is a very important step in the manufacturing of composites and nanocomposites made with unsaturated polyester resin (UP). The cure reaction must proceed in a carefully controlled state in view of achieving a good product quality in many aspects. The cure reaction of pure UP resins is usually exothermic and the high temperature will always cause adverse damage to its final product; hence the controlling of the exothermic heat is of paramount importance in the curing reactions.

The cross-linking reaction of polyester resin is a free radical chain growth copolymerisation. The polyester oligomer provides cross-linking points for network formation, while styrene monomer provides linear chain extension. Gel time measurement is a suitable tool to study curing.

Considering that a tridimensional structure will develop soon after the initiation of free radical curing, it is important to be able to understand how the induction process will depend on the initiator systems, the control of gelation as well as curing rate for polyester resins to their use in various applications. A review of the data in the literature shows that there are some references, so that the increase in methyl ethyl ketone peroxide and promoter cobalt naphthenate causes a decrease in gel time [5, 6]. Yang et al. [7] correlated the curing conditions such as curing temperature, initiator concentration, and acceleration concentration with the gelation.

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The combination of a filler with a resin leads to a new product with new properties. Some of all of these changes are advantageous but others are less favourable [8]. Kubota [9] reported that the presence of a high quantity of filler in the cure system increased both the thermal conductivity and the viscosity of the resin; however, it reduced the concentration of reactive double bonds per unit volume. The first two factors enhanced the cure reactions, the last factor had an unfavourable effect on cure. According to his observations, with increasing filler content the cure started at a lower temperature; however, the total heat of cure decreased with increasing filler content. Lucas and co-workers [10] reported a decrease in the induction period of the styrene/ polyester system cured in the presence of $CaCO_3$, as a filler. This effect was attributed to preferential adsorption of inhibitors, including dissolved oxygen, in the filler-rich phase. McGee [11] applied a simple nth order model to demonstrate the effect of particulate fillers on the heat transfer and cure process. He reported that the gel time of polyester system increased with increasing the glass content.

Since both the gel time and the maximum exothermic temperature required for a thermoset reactive plastic composition change according to the volume of product added together at one time, it is important to note the volume in all calculations. By selecting an adequate volume will permit gel time and peak exothermic temperature data to be collected in a satisfactorily accurate as well as reproducible way, or to conduct application evaluation, quality control, and material characterization of a thermosetting plastic composition.

This work focuses on establishing, in a more or more approximate manner, the typical curing times via a gradual change in the amounts of methyl ethyl ketone peroxide, cobalt octoate and a charge coming from waste from the ceramics industries, with the ultimate purpose of developing new products on the basis of the charge and the unsaturated polyester resin.

2. Materials and methods
2.1. Material preparation
Methyl ethyl ketone peroxide (MEKP), cobalt octoate (Co) and porcelain powder (PP) were employed as initiator, accelerator and filler.

The resin used was a commercial general-purposeorthophtalic polyester resin with medium reactivity and the styrene content was 34%.

Ceramic sanitary wares, such as basins, toilets, bathrooms, and sinks, were collected from public landfills in Settat, Morocco. These devices were broken with a hammer and crushed in a crusher to obtain a granular material with particles smaller than 4 mm in diameter. The ceramic waste was then dry milled in alumina media (30% alumina balls, 30% ceramic waste, and 40% air) for 30 min to obtain a ceramic powder. Ceramic powders (PP) with a particle size <180 μm were chosen for this investigation.

2.2. Experimental method
2.2.1. Curing procedure
The resin or resin filler was prepared by adding the required amount of initiator at ambient; next, the required dose of accelerator was applied and the mixture was mixed shortly afterwards. The gel time was established by manual stirring from time-to-time. At all times, the curing exotherm was obtained by positioning a thermocouple in the centre of an adequate quantity of catalysed resin or resin filler in a glass specimen and initially kept at room temperature. In view of achieving more representative data, a large series of experiments with catalyst level (1-2wt%), initiator level (0.12-1wt%) and porcelain powder ammount (0-50wt%), as the other test conditions, need to be as close as possible to the conditions in which the material is prepared. Table 1 shows the different experiments carried out during this study.

2.3. X-Ray Diffraction
Diffraction data were collected at room temperature on a Phillips D 5000 ($\theta - \theta$).

Diffractometer operated at 40 kV and 40 mA with Bragg–Brentano geometry and Cu Kα radiation (α= 1.54056 Å). The patterns were scanned with a step size of 0.01° (2θ) in the 2θ range of 10–80°.

In order to identify and understand the structure of the samples prepared, we have realized a series of X-ray diffraction tests on powder samples (Figure 1).
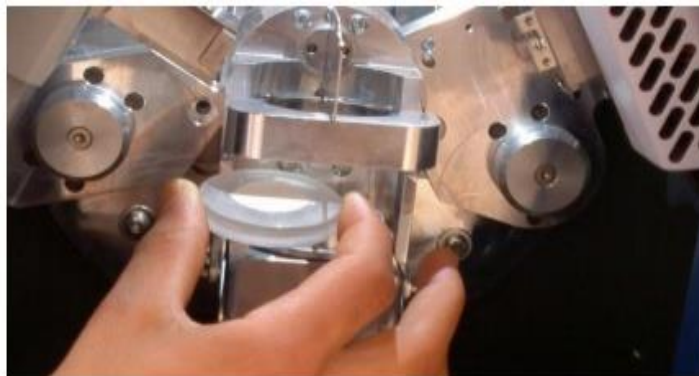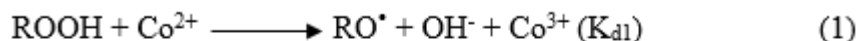

Figure 1. Photo example of a sample during X-ray analysis

3. Results and discussions
3.1. Curing process results
3.1.1. Importance of methyl ethyl ketone peroxide

Figure 2 shows thermograms of an unsaturated polyester resin cured isothermally at room temperature utilizing different amounts of MEKP and Co. The impact of the initiator on curing process is clear. For instance, induction period shortens as the amount of MEKP increases. This is due to the increasing decomposition of MEKP molecules and the rapid production of alkoxy and peroxy radicals that initiate polymerization reactions as described in the kinetic diagram.

$$ROOH + Co^{2+} \longrightarrow RO^{\bullet} + OH^{-} + Co^{3+} \; (K_{d1}) \qquad (1)$$

$$ROOH + Co^{3+} \longrightarrow ROO^{\bullet} + H^{+} + Co^{2+} \; (K_{d2}) \qquad (2)$$

Results of the gel time in Figure 3 and Table 1 support the accelerated reaction due to the increased concentrations of peroxide. This is primarily due to an increase in free radicals generated by the accelerator's decomposition of the catalyst.

The free radicals cause the exothermic copolymerization process to start. During free radical polymerisation, the resulting heat leads to an increase in temperature. As a result, the accumulation of heat causes an increase in the speed and the molecular weight of the polymer. As indicated by equation (1), gel time is inversely dependent on initiator level over the majority of the initiator range studied, which is consistent with gel time results of other workers [6, 12].

Table1. Effect of recycled ceramic waste (PP) content, MEKP and Co on curing characteristics (gel time (t_{gel}) and time to peak (t_{max})) and Peak Temp (T_{max})

MEKP + Co + PP (%)	Parameter		
	t_{gel} (min)	t_{max}(min)	T_{max} (°C)
2 + 0.5 + --	06.30	11.00	190
1.5 + 0.5 + --	09.15	13.30	170
1 + 0.5 + --	13.00	19.30	165
2 + 0.12 + --	09.15	13.4	180
2 + 0.5 + --	06.30	11.00	190
2 + 1 + --	04.45	09.15	189
2 + 0.5+ 28.5	09.45	15.45	146
2 + 0.5 + 41	10.15	16.30	136
2 + 0.5 + 50	13.00	18.30	123
2 + 0.12 + --	09.15	13.45	180
1.5 + 0.12 + --	16.15	21.45	168
1 + 0.12 + --	17.15	22	164

MEKP + Co + PP (%)	Parameter		
	t_{gel} (min)	t_{max} (min)	T_{max} (°C)
1.5+ 0.12 + --	16.15	21.45	168
1.5 + 0.5 + --	09.15	13.30	170
1.5 + 1 + --	08.15	12.30	177
1.5 +0.5+28.5	13.30	17.00	122
1.5+ 0.5 + 41	14.30	17.45	119
1.5 + 0.5 + 50	16.00	19.15	117
2 + 1 + --	04.45	9.15	189
1.5 + 1 + --	08.15	12.30	177
1 + 1 + --	11.00	18.00	169
1+ 0.12 + --	17.15	22.00	164
1 + 0.5 + --	13.00	19.30	165
1+ 1 + --	11.00	18.00	169
1+ 0.5 +28.5	16.00	27.00	136
1 + 0.5 + 41	23.45	28.15	118
1 + 0.5 + 50	25.30	30.45	120

Figure 2. Measured exotherm of the unsaturated polyester
resin containing various levels of MEEK and Co at. 20 °C

3.1.2. Importance of cobalt octoate

In general, an increase in the level of the MEKP and Co system leads to an increase in the reaction rate. For an example, analysis of the data obtained shows that the gel time is in the interval (6.3-13) for the MEEK+Co mixture when it varies in the interval (2 + 0.5 /1 + 0.5). In addition, the time varies from 04.45 for (2 + 1 + --) to 11 for (1 + 1 + --).

In Table 1, an interesting observation of the influence of cobalt concentration on gel time and exothermic temperature can be seen. As the concentration of cobalt increases, the gel time is decreased due to the increase in the number of activated resin groups. These results are in good agreement with the literature [6, 7, 12].

It can be noted that, the increase in accelerator level does not contribute significantly towards T_{max} at higher levels of catalyst.
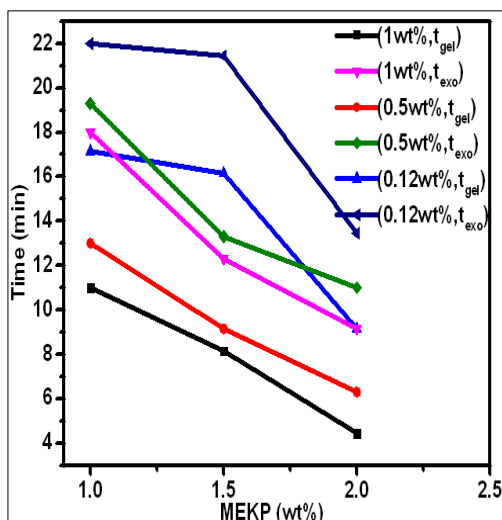
Figure 3. Gel time and time to peak vs MEKP at different level of Co

Cross-linking of the resin takes place at an earlier stage, which results in a shorter curing reaction and, therefore, a smaller gel time and a greater viscosity. As the viscosity of the resin increases, the chains have the impression not to move. As a result, the system will require an additional amount of energy to help not only the chain mobility but also the curing reaction.
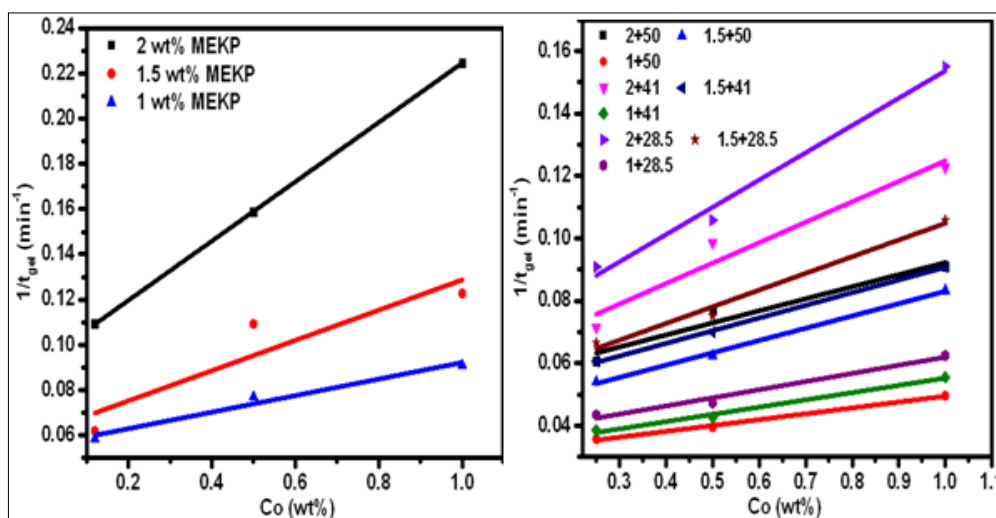

Figure 4. Reciprocal gel time vs. Co at different level of MEKP

Figure 4 shows the relationship between cobalt concentration and gel time, where $(t_{gel})^{-1}$ is illustrated as a function of the weight percent of cobalt. As we can see in the figure, linear plots have been obtained, where the intercepts are very close to zero, and the slope increases with increasing MEKP. The observed linear behaviour is related to which will be explained later.

It has been demonstrated that the initial concentration of initiator, catalyst, and induction period are related by the equation [13]:

$$t_z = \frac{[Z]_0}{k_d[ROOH][Co^{2+}]} \tag{1}$$

For periods longer than t_z, the free radicals react with the monomers and produce heat. Furthermore, eq. (1) predicts a linear relation, as shown in Figure 4, for all formulations; with the correlation coefficient take the values of 0.974, 0.86 and 0.99 for 1, 1.5 and 2 wt% of MEKP.

3.1.3. Importance of porcelain powder

The research study is dedicated to the effects of the porcelain powder on the cure of the UPR resin. For this purpose, various mass concentrations of the filler (PP) have been incorporated into the resin. They are 0, 28.5, 41 and 50wt%. Different mixtures have been experimented with varying levels of MEKP and Co.

The exothermal graph (Figure 5) indicates that the higher amount of PP causes a noticeable increase in the UPR resin response time. As a result, the gel time and the exothermic peak time increases with increasing weight percent of PP. On an opposite, the temperature of the reaction and therefore the exothermic peak temperature will decrease.

For the same mixture of filler and resin, the effect of the catalytic system is unchanged and respects the obtained results with no incorporation of the porcelain powder. The gel time is reduced from 25.3 to 11min for (1+0.5+50)to (1+0.5+--) and from 13 to 4.45 min for the resin when the catalytic system is changed from (2+1+--)to (1+0.5+--). This pattern is very similar and consistent for all compositions and is also generalized for the overall reaction time (Figure 6 and Table 1).
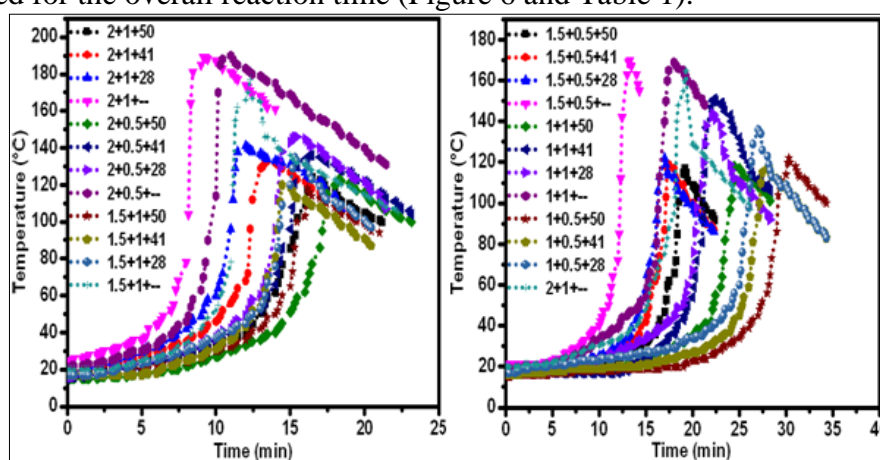

Figure 5. Measured exotherm of the unsaturated polyester resin containing X wt% initiator (MEEK), Y wt% cobalt and PP wt% at. 20°

The rise in gel time can be attributed to the retardation of the cross-linkage of the UPR and the absorption of the heat generated in the exotherm reaction. Rheological measurements carried out by Simitziz [5] showed that the inorganic fillers (talc, and quartz) lead to an increase in the gel time delaying the crosslinking of the UPR. They reported that the microgels formed cannot come close because they are impeded by the presence of the PP, with the consequence that the transition stage and then the macrogelation are retarded.
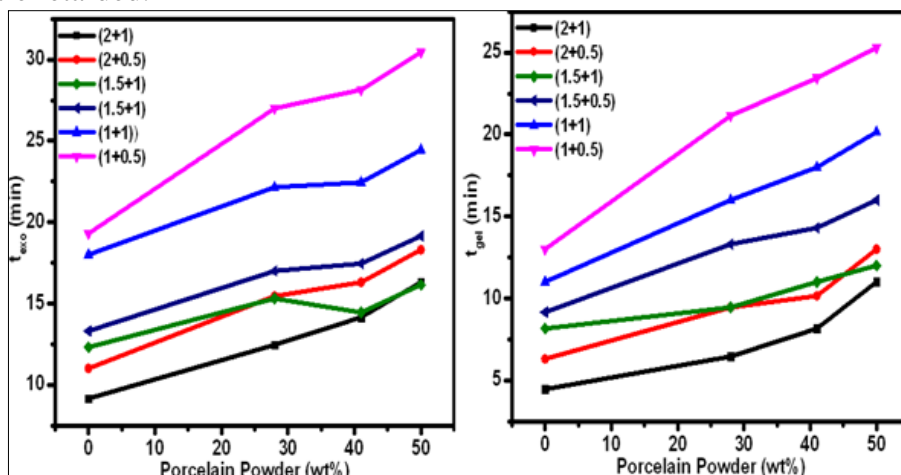

Figure 6. Gel time and time to peak vs. wt% of PP with different levels of MEKPand Co

As the amount of filler in the resin increases, so the gel time and the curing time increases. As a result, these experiments can be used to establish a range of time needed to prevent the gelation for the mixture and produce the material in a specific time period.

The gel time as a fonction of cobalt for the mixtures that contain 41 and 50 wt% has been investigated and the findings are presented in Figure 6. The relationship between $(t_{gel})^{-1}$ and the Cobalt-content is linear and fairly perfect with a Correlation Coefficient higher than 0.95. The slope and the intercept are increasing as the peroxide level increases and diminishing as the PP level increases. these observations are in good accordance with the preceding data. Changes in the decomposition mechanism of the initiator that affect the curing process may occur when the initiator concentration is very high.

It is interesting to note that, for the MEKP initiated system, the gel time extrapolates to an infinite value at zero concentration of added cobalt salt, which may result from self decomposition of the peroxide or by the accelerating decomposition of the peroxide bycatalytic impurities in the resin, in agreement withother workers [6, 14].

Figure 7 and the Table 1 depict in a qualitative and quantitative manner the effects of increasing weight percent of PP in formulation on the exothermic temperature and the temperature of the various mixtures. Hence, the experimental findings indicate that the reaction temperature also reduces as the charge is gradually increased.
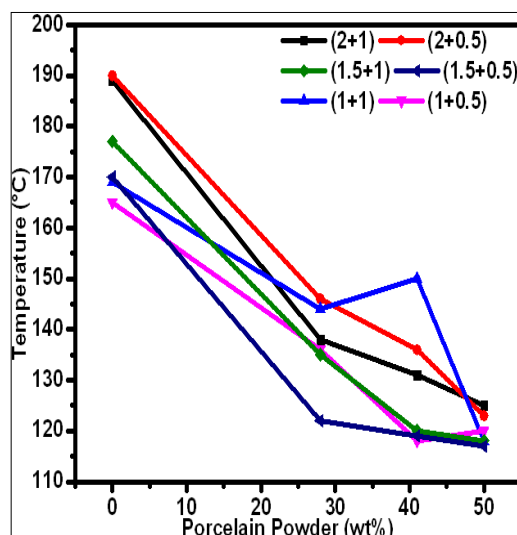

Figure 7. Temperature vs wt; PP at different combination of MEKP and Co

As the decomposition of free radicals contributes towards an increases of heat accumulation, the presence of PP absorbs the heat in reaction.

In previous work, the authors examined the action of fillers on the curing kinetics of an epoxy/anhydride resin. They concluded that the total heat of reaction reduces with the addition of fillers; hence, the fillers adsorb the monomers reacting on their surface, affecting the stoichiometry and create a steric barrier to the forming network [15].

However, to investigate this in depth, further research, such as FTIR and DSC studies, are necessary to understand these effects.

3.2. X-Ray Diffraction results

In order to determine the effect of the ceramic filler on the curing process, we carried out a crystallographic study on porcelain powder (PP), neat resin (UPR) and with different weight fractions of PP ranging from 10, 20, 30, 40 and 50 wt%, with 2wt% of MEKP and 1wt% of Cobalt Octoate.
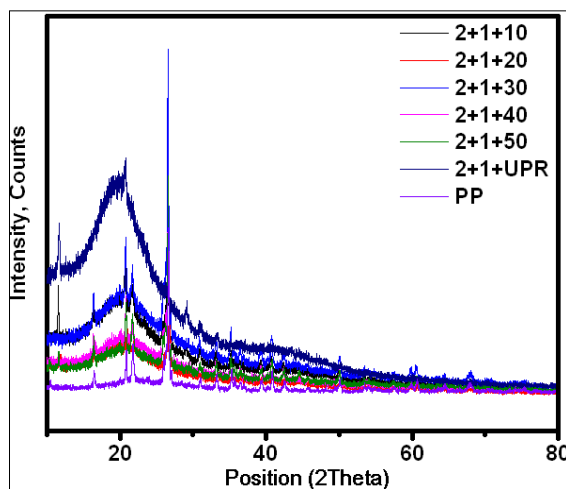
Figure 8. Typical powder XRD patterns of resin, PP
and samples with 10, 20, 30, 40 and 50wt% of PP

In Figure 8, it can be seen that the recycled ceramic powder presented mineral phases typical of a fired ceramic material, principally quartz and to a lesser extent, mullite, and other impurities. In addition, X ray spectra of porcelain powder (PP) exhibit a structure comparable to that of crystalline systems while the composite (CP) developed has a semi-crystalline nature due the amorphous nature of the UPR.

Finally, the XRD study of crystalline phases present in the new materials produced the results shown in Figure 8. Here, it can be seen that the all materials developed presented the phase typical of the PP. Also evident is the presence of semi-crystalline phase, resulting from mixing the porcelain powder and UPR, thus indicating that the porcelain powder incorporated into the mix did not interfere with the UPR curing process.

Finally, it has been noted that it is considerably more complex to use the gel time as a characteristic parameter of a material due to the large variety of procedures based on the evaluation of various physico-chemical processes. Nevertheless, the improved instrument base and detailed studies of the processes taking place in curing systems are contributing to the appearance of new methods for the determination of the gel time, which are outstanding in terms of both their methodological accuracy and high reproducibility [16].

4. Conclusions

Several experiences of cure reactions have been studied in order to determine the gel time, the curing time and the exothermic temperature of the cured resin at room temperature. The main results are the following.

When the initial concentration of the initiator and accelerator are lower, the cure rate becomes significantly slower as the concentration of radicals in the curing system is reduced. The exothermic temperature is increased with the level of MEKP.

An increase in the porcelain powder rate will cause an increase in gel time and cure time. On a contrary, it reduces the exothermal temperature.

The modification of the added amount of PP proved to be effective in prolonging the gel time. However, the increase in the amount of PP added also significantly delayed the cure rate, and the decrease in temperature.

In accordance with the above test results, the porcelain powder just retards the curing process and is not chemically reacted with the resin.

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