Composition and Properties of Triple Superphosphate Obtained from Oyster Shells and Various Concentrations of Phosphoric Acid

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ABSTRACT: Triple superphosphates [TSPs, Ca(H$_2$PO$_4$)$_2$·H$_2$O] were produced by exothermic reactions of oyster shells and different concentrations of phosphoric acid (10, 20, 30, 40, 50, 60, and 70% w/w) in a molar ratio of 1:2. The percentage yields, P$_2$O$_5$ and CaO contents, metal impurities, and thermal behaviors of all the as-prepared products are dependent on the concentrations of phosphoric acid added during the production processes, which confirm to get the best optimum of 60% w/w phosphoric acid. All the as-prepared products were characterized by several characterization methods [X-ray fluorescence, thermal gravimetric/derivative thermal gravimetric analysis, powder X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy], verifying that all the obtained compounds are TSP that can be used as fertilizers without metal toxic contaminants. From the successful results, the method for TSP production can be applied in the fertilizer industry based on starting waste materials of oyster shells that can replace the use of unsustainable phosphate or calcium minerals obtained from nonliving things.

1. INTRODUCTION

Triple superphosphate [TSP, Ca(H$_2$PO$_4$)$_2$·H$_2$O], also known as concentrated superphosphate in North America and monocalcium phosphate monohydrate (MCPM), is a chemical fertilizer material with a phosphorus content of over 40%, measured as phosphorus pentoxide (P$_2$O$_5$). TSP fertilizers are generally obtained by adding phosphoric acid to phosphate rock, mainly fluorapatite, according to reaction 1:

$$\text{Ca}^{10+}\text{(PO}_4)_{2}\text{X}_2(\text{s}) + \text{14H}_2\text{PO}_4(\text{aq}) + \text{10H}_2\text{O}(\text{l}) \rightarrow \text{10Ca(H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O(s)} + \text{2Y}(\text{l})$$

where X = OH$^-$ or F$^-$ and Y = H$_2$O or HF.

TSP has been enormously used in agriculture all over the world, causing the phosphate rock reserves to deplete and prices increased by 300%. Recently, TSPs have also been utilized to reduce the acidity of tropical acid soil, alleviate arsenic toxicity in rice, phytostabilize Pb–Zn mine tailings, cultivate Chlorella pyrenoidosa, grow bermudagrass, produce white oyster mushroom (Pleurotus ostreatus), sustain soil fertility and improve nodulation, produce ceramics, produce hardening composite materials, and produce bioactive composite bone cements. Other TSP studies include improving phosphate solubility in soil using Trichoderma spp., preparation of slow-release TSP fertilizers, and investigation of the potential to breed for maize hybrids under reduced P starter fertilizer. Another researched method for producing TSP has been via monetite from brushite by using sonication. The disadvantages for...
producing TSP fertilizer from phosphate rock are purity, insolubility, and reduction of natural mineral resources. Therefore, it is necessary to find another raw material to replace phosphate rock, such as calcium carbonate obtained from limestone minerals or various shells/eggshells.

This research focused on oyster shells because oyster is one of the popular kinds of seafood all over the world. In Thailand, the number of oyster shells is enormous with over 300,000 tons generated annually. Oyster shells are biological wastes, which are mainly composed of calcium carbonate, 

\[ \text{CaCO}_3 \] (min. 96%), and minor amounts of other impurities. Oyster shell wastes have been dumped into the coastal waters and landfills, an increasingly serious environmental hazard. Various attempts have been made to reduce their environmental impacts, including using them as the calcium source. In this research, we have studied to use renewable raw materials such as oyster shells and developed a new process to reduce the cost of TSP production. Using this method, the cost of calcium carbonate obtained from oyster shells is very low when compared with that from phosphate rock ore. Additionally, the utilization of oyster shell waste is beneficial to reduce the environmental toxicity and save the natural resources such as limestone and phosphate rock ore for the next generations.

The aim of this report is to present a great potential to convert oyster shell waste into a value-added product using a simple and effective approach. Oyster shell powders were used as the calcium source to produce TSP fertilizer products by adding different concentrations of phosphoric acid in the range of 10−70% w/w. All the as-prepared products were analyzed by several methods including X-ray fluorescence (XRF), X-ray diffraction (XRD), infrared (IR), thermogravimetry/derivative thermogravimetry (TG/DTG), and scanning electron microscopy (SEM) to verify that the obtained target compounds were truly TSP that can be used as fertilizers without metal toxic contaminants.

2. RESULTS AND DISCUSSION

2.1. Production Results. The preparation conditions and percentage yields of TSP products obtained from the reaction between oyster shell powders and different concentrations of phosphoric acid are given in Table 1. When the concentration of phosphoric acid increased, the degree of the exothermic reaction increased as well. As a result, preparation methods with higher concentrations of phosphoric acid caused the powder to rapidly dry. For example, for TSP70, it took only 3 h. With the low concentrations of phosphoric acid used, low percentage yields of the product were obtained because there were inadequate amounts of phosphoric acid to react with the oyster shell. This resulted in the mixed phases of calcium carbonate and superphosphate, which will be discussed and confirmed by TGA, Fourier-transform IR (FTIR), and XRD data in the next parts. The synthesized powder that has the highest percentage yield was TSP60 (94.62%), while TSP70 which used 70% w/w phosphoric acid gave the percentage yield of only 71.77%. This effect may be related to the number of water molecules in the crystal structure because the strong exothermic reaction occurred in the preparation process for TSP70, which will be explained in TGA, XRF, and XRD information. On the basis of production, the short preparation time and highest percentage yield are the preferred features and, in this research, it was the reaction between 60% w/w phosphoric acid and oyster shell powder (\( \text{CaCO}_3 \)) with the molar ratio of P/Ca = 2/1.

2.2. X-ray Fluorescence. Chemical compositions of all the as-prepared samples are presented in Table 2. The seven synthesized superphosphates (TSP10−TSP70) contain large proportions of phosphorus pentoxide (41.40−77.54%) and calcium oxide (18.20−35.70%) and minor oxide impurities (\( \text{SiO}_2, \text{K}_2\text{O}, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{and} \text{SO}_3 \)). The quantities of the minor oxide impurities decreased from TSP10 to TSP60 samples, but they increased in the TSP70 sample. This result indicates that concentrated phosphoric acid can leach the oxide impurities that were specific to some ranges and the best concentration for preparation was 60% w/w phosphoric acid, which was revealed by much less contained impurities. The observed phosphorus pentoxide contents in the range of 60.40−77.54% for the six obtained superphosphates (TSP20−TSP70) were higher than that of TSP in the fertilizer industry (40−58%) and other research works. For the quantity of calcium oxide in TSP fertilizer, the theoretical value is 22.22% and the previous works were reported as 20−22%, which are close to the observed values (18.20−19.70%) of TSP30−TSP60 samples. The high calcium oxide contents of 35.70% for TSP10, 24.70% for TSP20, and 31.00% for TSP70 indicated that solid phases of calcium carbonate, dicalcium phosphate dihydrate, and MCPM have been mixed, which were supported by the P/Ca molar ratio obtained at below 1.0. For the P/Ca molar ratio of TSP fertilizer, the theoretical values and previously reported works were found to be in the range of 1.5−2.5 and the TSP30−TSP60 samples were found to have ratios in this range (1.48−1.67). From these obtained XRF data, the much fewer the impurities, the higher the \( \text{P}_2\text{O}_5 \) content, and the P/Ca molar ratio in the range of 1.5−2.5 was used as a basis for the selection of 60% w/w phosphoric acid as the optimum concentration. The obtained results of XRF well support the production results. Additionally, TSPs obtained from oyster shell powder in this work did not have the contents of toxic trace elements (Cr, Sr, Cd, etc.), unlike TSPs produced from phosphate rock ore.

2.3. Thermal Analysis. The TG/DTG thermograms of all the as-prepared samples are shown in Figure 1. The TG traces (Figure 1a) illustrate percentage mass losses in the range of 30−800 °C, which are related to DTG peaks (Figure 1b), indicating the decomposition mechanism of reactions. The TG/DTG curves observed were similar for the samples of...
TSP20 and TSP70, TSP30 and TSP50, and TSP40 and TSP60, whereas the TG/DTG curves of TSP10 were significantly different from other results. At a temperature below 100 °C, the mass losses and DTG peaks observed in all the as-prepared samples were assigned to the dehydration of moitures. The TG curves of the TSP10 sample appear in the range of 100−200, 480−520, and 650−750 °C corresponding to DTG peaks at 140, 186, 518, and 706 °C, which were related to the first two steps of dehydration, deprotonation of hydrogen phosphate, and decarbonation reaction, respectively. The total mass loss was about 23% which corresponded to the retained mass of about 77%, which confirmed that this prepared sample was the mixed solid phases of CaCO3 and calcium phosphates [CaHPO4·2H2O and Ca(H2PO4)2·H2O].

The TG curves of the TSP20 and TSP70 samples were similar in the range of 100−200 and 300−400 °C corresponding to four DTG peaks at 140, 186, 217, and 330 °C, which were related to the first two steps of dehydration, deprotonation of hydrogen phosphate, and decarbonation reaction, respectively. The total mass loss was about 23% which corresponded to the retained mass of about 77%, which confirmed that this prepared sample was the mixed solid phases of CaCO3 and calcium phosphates [CaHPO4·2H2O and Ca(H2PO4)2·H2O]. The TG curves of TSP20 and TSP70 samples were similar in the range of 100−200 and 300−400 °C corresponding to four DTG peaks at 140, 186, 217, and 330 °C, which were related to a mass loss of about 17% (the retained mass of about 83%). The TG curves of TSP30, TSP40, TSP50, and TSP60 samples appeared similarly in the range of 100−200 and 300−400 °C corresponding to four DTG peaks at 140, 186, 217, and 330 °C. The total mass losses (the respective retained mass) were found to be 21 (79%), 22 (78%), 24 (76%), and 24% (76%), respectively. The total mass losses of the TSP30 and TSP40 samples were close to the theoretical value (21.43%, 3 mol H2O) of Ca(H2PO4)2·H2O while those of the TSP50 and TSP60 samples were more than 3% because moitures were absorbed, which can be seen from their TG traces at below 100 °C. Additionally, the total mass losses of the TSP20 and TSP70 samples were lower than the theoretical value because impurities were mixed in the target compound [Ca(H2PO4)2·H2O], which must be discussed clearly. Basically, thermal transformation reactions of the target compound, TSP [Ca(H2PO4)2·H2O], that included two reactions, dehydration and deprotonation of hydrogen phosphate, produced the final decomposed product calcium polyphosphate [Ca(PO3)2] at 600 °C according to reactions 2 and 3:

\[
\text{1st: } 100 - 250 °C \quad \text{Ca(H2PO4)_2 \cdot H_2O} \rightarrow \text{Ca(HPO}_4)_2 \cdot H_2O + \text{H}_2\text{O} \quad (2)
\]

\[
\text{2nd: } 250 - 400 °C \quad \text{Ca(HPO}_4)_2 \rightarrow \text{Ca(PO}_3)_2 + 2\text{H}_2\text{O} \quad (3)
\]

For the obtained thermal analysis results of the TSP20−TSP70 samples, each reaction of 2 and 3 was separated into two steps because of the distinct environment of the water molecule and dihydrogen phosphate anion in the structure of the as-prepared samples. The thermal transformation reactions are proposed as follows:

\[
\text{Ca(H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O} \rightarrow \text{Ca(H}_2\text{PO}_4)_2 \cdot y\text{H}_2\text{O} + n\text{H}_2\text{O} \quad (4)
\]

\[
\text{Ca(H}_2\text{PO}_4)_2 \cdot y\text{H}_2\text{O} \rightarrow \text{CaH}_2\text{PO}_4 + y\text{H}_2\text{O} \quad (5)
\]

\[
\text{Ca(H}_2\text{PO}_4)_2 \rightarrow \text{CaH}_2\text{PO}_4 + \text{H}_2\text{O} \quad (6)
\]

### Table 2. Chemical Compositions of the As-Prepared Samples Obtained from the Reaction between Oyster Shells and Various Concentrations of Phosphoric Acid [10 (TSP10), 20 (TSP20), 30 (TSP30), 40 (TSP40), 50 (TSP50), 60 (TSP60), and 70% (TSP70) w/w] by XFS

| samples     | P2O5 (%) | CaO (%) | SO3 (%) | K2O (%) | Fe2O3 (%) | Al2O3 (%) | SiO2 (%) | P/Ca mole ratio |
|-------------|----------|---------|---------|---------|-----------|-----------|----------|----------------|
| oyster shell| 1.065    | 75.950  | 0.775   | 0.277   | 1.077     | 2.871     | 18.257   |                |
| TSP10       | 41.400   | 35.700  | 0.712   | 0.268   | 0.942     | 2.870     | 18.110   | 0.46           |
| TSP20       | 60.400   | 24.700  | 0.630   | 0.193   | 0.502     | 2.690     | 10.890   | 0.96           |
| TSP30       | 74.100   | 19.700  | 0.432   | 0.217   | 0.431     | 2.220     | 3.120    | 1.48           |
| TSP40       | 77.200   | 18.200  | 0.429   | 0.197   | 0.354     | 1.230     | 2.590    | 1.67           |
| TSP50       | 76.840   | 19.300  | 0.417   | 0.347   | 0.340     | 0.571     | 2.530    | 1.57           |
| TSP60       | 77.540   | 18.700  | 0.403   | 0.340   | 0.340     | 0.545     | 2.480    | 1.64           |
| TSP70       | 61.800   | 31.000  | 0.602   | 0.107   | 0.458     | 0.723     | 5.370    | 0.79           |

Figure 1. TG (a) and DTG (b) curves of Ca(H2PO4)_2·H2O produced from oyster shells and phosphoric acid with concentrations of 10 (TSP10), 20 (TSP20), 30 (TSP30), 40 (TSP40), 50 (TSP50), 60 (TSP60), and 70% (TSP70) w/w.
\[
\text{CaH}_2\text{P}_2\text{O}_7 \rightarrow \text{Ca}(\text{PO}_4)_2 + \text{H}_2\text{O} \tag{7}
\]

\((n = x + y = 1)\).

The number of thermal transformation steps may be less than two steps (reactions 2 and 3) because of the overlapping reactions caused by close heating energy for the eliminated crystal water molecules with similar environments in the structure. On the other hand, the number of thermal transformation steps could also be more than two steps because of the splitting reactions caused by different distinct crystal water molecules in the structure affecting the energy used differently to break bonds. In general, the different thermal transformation behaviors for the compounds of the same formula can occur depending on different parameters such as the methods of preparations, reagents, synthesis conditions, and so forth.\(^{35,36,38}\) The thermal analysis results obtained clearly indicated that the thermal behaviors of TSPs were affected by the concentrations of phosphoric acid during their preparation.

2.4. IR Spectroscopy. The traditional method for the identification of material compounds is using IR absorption spectrum (FTIR) based on the identification of chemical functional groups contained within the molecules of the as-prepared compounds. The target compound synthesized is the general chemical formula of Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O} that is well known in the fertilizer field as TSP and in the academic field as MCPM. This target compound contains the block units of CaO, \([\text{H}_2\text{PO}_4]^-\) ion, and H\(_2\)O molecule within the structure. Therefore, all spectra of the prepared samples will be identified based on the fundamental vibrational modes of these molecules.\(^{37}\) The characteristic frequency bands of Ca–O bonds are observed at around 877, 720, and 500 cm\(^{-1}\). The fundamental vibrational modes of the \([\text{H}_2\text{PO}_4]^-\) ion include the bending of O–P–O, the P–O stretching, in-plane P–O–H, and out-of-plane P–O–H, which are observed in the region of 600–450, 1100–900, 1250–1200, and 900–800 cm\(^{-1}\), respectively.\(^{29,35}\) The fundamental vibrational modes of H\(_2\)O molecules consist of three bands: bending, symmetry, and asymmetry stretching of H–O–H bonds, which appear at 1630, 3100, and 3340 cm\(^{-1}\), respectively.\(^{8,29,35}\) Additionally, the bands at center that include 2980, 2875, 2513, and 794 cm\(^{-1}\) are harmonic vibrations of these elongation modes.\(^{35,38}\)

The FTIR results of all prepared samples show fundamental vibrations of the block units that are within the Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O} structure, resulting in their similar spectra (Figure 2).\(^{35}\) The FTIR spectra of TSP30, TSP40, TSP50, and TSP60 samples are very closely similar and resemble that of Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O} reported in the previous literature,\(^{35}\) while the FTIR spectra of TSP10 and TSP20 samples show double peaks at 3400–3600 cm\(^{-1}\), corresponding to the O–H bonds matching with a low concentration of HPO\(_4^{2-}\) in the sample. This indicates that the TSP10 and TSP20 samples are the mixed solid phases of CaHPO\(_4\)\cdot2H\(_2\)O and Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O} in the structure. Furthermore, the FTIR spectrum of the TSP70 sample is different from the other spectra at over 3000 cm\(^{-1}\), showing a broad band that can be assumed in the same way.

2.5. X-ray Diffraction. Figure 3 shows the X-ray diffractograms of all the as-prepared samples. The XRD patterns of TSP30, TSP40, TSP50, and TSP60 were shown quite similar, but intense peaks are different. There were two sharp characteristic peaks at 2\(\theta\) = 22.95 and 24.18\(^{\circ}\) corresponding to (021) and (120) reflections for the anorthic crystal structure of Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O}, respectively.\(^{36}\) According to the standard data PDF\# 700090, the T-labeled diffraction peaks can be indexed, which confirms that the as-prepared Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O} crystal structure is in the anorthic system with the space group \(\text{P}_{\text{h}}\text{1}\text{a}\).\(^{8,29}\) For the XRD patterns of TSP10, TSP20, and TSP70, the four observed strong intense peaks at 2\(\theta\) = 11.95, 21.09, 26.91, and 29.38\(^{\circ}\) are related to (100), (200), (002), and (210) reflections, respectively, for the crystal structure of CaHPO\(_4\)\cdot2H\(_2\)O, which are indexed by using the standard data PDF\#72-0713.\(^{38}\) Furthermore, the sharp peaks at 2\(\theta\) = 56.05\(^{\circ}\) appeared in the patterns of TSP10 and TSP20 samples, which are reflected for the crystal structure of CaHPO\(_4\)\cdot2H\(_2\)O.\(^{38}\) The XRD results obtained indicate that mixed phases between CaHPO\(_4\)\cdot2H\(_2\)O and Ca\((\text{H}_2\text{PO}_4)_2\)\cdot\text{H}_2\text{O} occurred in the samples of TSP10, TSP20, and TSP70.\(^{36,38}\) They could be dependent on different concentrations of phosphoric acid from the preparation process. The FTIR and XRD results obtained are well consistent.

2.6. Structure and Morphology of Superphosphates. Figure 4 shows the SEM micrographs of all the prepared samples. The SEM micrograph of TSP10 (Figure 4a) shows some chip-like woods with various large and small pieces horizontally. The SEM micrograph of TSP20 (Figure 4b)
shows some sheet-like woods with various sizes and shapes in different directions. The SEM micrographs of TSP30, TSP40, TSP50, TSP60, and TSP70 samples (Figure 4c–g) show a group of polyhedral sheet-like fragments with different particle sizes of about 2–10 μm. Morphologies of TSP30, TSP40, TSP50, TSP60, and TSP70 samples have a homogeneous microstructure in which the particle size tends to decrease with the increasing phosphoric acid concentration. It can be
deduced that the product morphologies were influenced by the concentration of phosphoric acid.

3. CONCLUSIONS

TSPs $[\text{Ca(H}_2\text{PO}_4 \text{)}_2 \cdot \text{H}_2\text{O}]$ were effectively produced by using oyster shells and different concentrations of phosphoric acid, and all products obtained had a relatively high P$_2$O$_5$ content of more than 40% without any toxic trace elements but with some minor elements for growing plants. The percentage yields, chemical contents, and thermal properties of the as-prepared products were dependent on the concentration of phosphoric acid added to oyster shells. The optimum concentration of phosphoric acid was 60% w/w supported by the obtained data with a highest yield and P$_2$O$_5$ content and fast production time. The use of these as-prepared compounds as fertilizers will provide the largest quantity of available phosphorus with a number of minor elements useful for plants. It will also environmentally help removing oyster shell wastes. This work adds valuable information for the improvement of TSP production for the fertilizer industry based on starting waste materials of oyster shells, replacing phosphate ores or calcium minerals obtained from nonliving things which are limited resources.

4. EXPERIMENTAL SECTION

4.1. Raw Material Preparations. The oyster shells were collected from a shell dumping place in Sriracha district, Chonburi Province, Thailand. Oyster shells were cleaned using saturated sodium hypochlorite solution until meat particles were removed. The cleaned shells were dried in an oven at 110 °C for 1 h. After that, the oyster shells were ground to obtained oyster shell powders with a particle size of 100 meshes (approximately 140 μm) as a raw material.

Industrial-grade concentrated phosphoric acid (85% w/w) was used without further purification. This concentrated acid was diluted with deionized water to prepare seven concentrations of phosphoric acids (10, 20, 30, 40, 50, 60, and 70% w/w). It shall be noted that the dilutions were strongly exothermic, so the solutions were left to cool down before further use.

4.2. Production of TSPs $[\text{Ca(H}_2\text{PO}_4 \text{)}_2 \cdot \text{H}_2\text{O}]$. The target compounds, TSPs $[\text{Ca(H}_2\text{PO}_4 \text{)}_2 \cdot \text{H}_2\text{O}]$ with different chemical compositions and properties, were synthesized based on the following replacement reaction

$$\text{CaCO}_3(s) + 2\text{H}_3\text{PO}_4(aq) \rightarrow \text{Ca(H}_2\text{PO}_4 \text{)}_2 \cdot \text{H}_2\text{O}(s) + \text{CO}_2(g)$$ (8)

For example, 58.17 mL of 10% w/w phosphoric acid was added into a beaker containing 10 g of oyster shell powder (CaCO$_3$). The mixed suspension was exothermic and stirred at 100 rpm until carbon dioxide was not evolved (up to 30 min). The pale yellow-white product obtained was dried at room temperature for 12 h and designated as TSP10. For other products, the process was repeated with different concentrations of phosphoric acids (42.19 mL of 20%, 26.31 mL of 30%, 18.53 mL of 40%, 13.97 mL of 50%, 11.01 mL of 60%, and 8.95 mL of 70% w/w) and the products were labeled TSP20, TSP30, TSP40, TSP50, TSP60, and TSP70, respectively. The yield of TSP considered according to reaction 8 was calculated by

$$\text{Yield (\%)} = \frac{m_{\text{obs}}}{m_{\text{theor}}} \times 100$$ (9)

where $m_{\text{obs}}$ and $m_{\text{theor}}$ are the mass of the obtained TSP powder in the preparation process from each phosphoric acid concentration and the mass of the TSP product calculated by theory, respectively.

4.3. Characterization. Chemical compositions of all the as-prepared samples were identified by an X-ray fluorescence spectrometer (Brand Model, City, Country). The structure and crystalline size of the as-prepared samples were identified by an X-ray powder diffractometer (Bruker AXS, Karlsruhe, Germany) with the Cu Ka spectral line ($\lambda = 1.54056$ Å) as the incident radiation. FTIR spectra were recorded by an FTIR spectrophotometer (PerkinElmer Spectrum GX, City, UK) from 4000 to 400 cm$^{-1}$ with 16 scans at a resolution of 4 cm$^{-1}$ by mixing 1 mg of the samples with 20 mg of KBr powder. TG/DTA (PerkinElmer Pyris Diamond, City, Country) was implemented to give the TGA curve of the sample in nitrogen gas from room temperature to 900 °C at a heating rate of 10 °C/min. Finally, surface morphologies of the superphosphate compounds were observed by a scanning electron microscope (Zeiss LEO VP1450, Oberkochen, Germany) after gold sputtering.

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Notes
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