The Utilization of MPCM Slurry for a Cooling System

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ABSTRACT: The present study has been conducted for manufacturing MPCM (microencapsulated phase change material) slurry with in-situ polymerization and proving their applicabilities for cooling system. The tetradecane as a core material of MPCM is coated with melamine. The produced capsules are observed by the optical microscope and SEM for superficial shapes and analysed their properties by DSC and particle size distribution by FA particle analyzer. It is found that narrow size distribution in 1 to 10 μm is resulted in 5 μm of average diameter and 9℃ melting temperature. The durability of MPCM capsules is tested with various types of pumps such as centrifugal, peristaltic, and mono. For the centrifugal and peristaltic pumps the breakage fraction of the capsules is resulted within 6% during 10,000 cycles, while the mono is over 8%. The cooling system, which has adopted MPCM slurry as a medium for transporting cold thermal energy, is designed to investigate the performance of newly developed coolant. The discharging times of cold energy in circulating 10 and 20 wt% MPCM slurry are lasted to 105 and 285 minutes, respectively.

Nomenclature

D_o : breakage fraction
L_o : initial MPCM thickness [m]
L_t : MPCM thickness after circulation [m]

1. Introduction

Microencapsulation techniques are most widely used in the development and production of improved drug-/food-delivery system. These techniques have normally advantages of enhancing material stability, reduce adverse or toxic effects, or extend material release for different applications in various fields of manufacturing. With the merit of delivery system without agglomeration of each particle contained in slurry, the microencapsulated phase change materials (MPCM) are used to store and transport the latent heat of PCM to the demand. MPCM applied for a cooling system of building has been under development in a pilot scale.(1-2) Recently, the ice ball types or ice slurry systems for adopting the latent heat of ice have been mostly used for the off-peak load cooling of building.

The production system of electricity in Korea has depended upon large scale power plants such as nuclear power and integrated combined cycle systems, etc., which require for the huge amount of new construction cost. In summer time during peak load of cooling, there is possibility of the power shortage due to load-follow operating system in the production of electricity, which is necessary of more power plant construction. On the other hand, in off-peak

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load period like the winter or at night time, power reserve rates rise up to 20% or more. If the demands are shifting the time of peak-load of electricity to the off-load period by using thermal storage system, it will contribute to saving a new construction cost of large scale power plants. Therefore, a well-regulated operating management of electricity is developed by using the thermal storage system.

Recently, the new technology of thermal storage system or materials is developed and investigated. For inducing the demands to avoid the power usage at a ceratin time, the government gives a benefit of applying for various utility rates between off-peak and peak lead period.

The thermal storage system (TSS) and its heat transportation have mainly stored the latent heat and supplied the sensible heat to the demands. In recent research, however, new materials transported by the latent heat such as, ice slurry, microencapsulated phase change materials (MPCM), micro-emulsion, and clathrate, are under development. The new technology is more effective than the conventional system applying for the sensible heat. That is, due to high thermal density, the system is resulted from compacting and cost saving. The heat transportation system by newly developed materials is approximately five times as much as the sensible supplying system in terms of heat density.

In the present research, MPCM technology is used to substitute for the conventional TSS system. MPCM slurry, which is encapsulated by paraffins such as tetradecane, can store and transport the latent heat. MPCM slurry has lots of advantages comparing to the sensible heat transportation system, ice slurry, and others. That is, the micro-sized paraffin is encapsulated by polymer like urea, nylon, melamin as surface materials. For the paraffin separated with water, the working fluid is transporting with high heat density without clogging and agglomeration, which are often ocurring serious trouble in ice slurry, micro-emulsion, and clathrate applied system. Also it could minimize heat loss during the transportation of MPCM slurry,(3-4) because the stored heat is transported with the segregated core by polymer. For the purpose of TSS and its transportation, in most researchers, microcapsule sizes are controled in the range of 1~100 μm, and also the surface materials such as synthetic or natural polymer are applied for their proper utilization.

In encapsulation process, monomer and polymer are carefully selected by their type, purpose, polymerization process. The physical and chemical properties of the produced MPCM slurry depend upon adopted materials and process.

The manufacturing process of microcapsules is well known in many areas, but complicated in the aspect of both basic chemistry and technology. This process is usually very complicate, since it involves various reactions and steps which take place at different phases. For example, the initial step of a simple coacervation-based process is based on adsorption of one of the wall-forming components onto the core materials-continuous phase interface.(5)

Based on the above mentioned micro-encapsulation processes, one of various encapsulation processes is selected and proper PCM within a certain temperature range and appropriate solid surface materials should be chosen to have the required physical and chemical properties of the capsules obtained. The produced MPCM slurry is used to apply for TSS and thermal transporting fluid, and it would change a conventional cooling system. And newly developed cooling system can improve many existing problems such as enhancing heat transfer by micro-convection due to entrained MPCM particles and applying thermal storage and transportation with one medium, and etc.(9-10)

In the present study, tetradecane, which has 5.8℃ melting temperature, is chosen as a core material and melamin-formaldehyde as its wall material is selected. Mass production system of MPCM slurry over 1 ton/batch are designed and constructed. And the produced MPCM slurry is applied for the cooling of a room with the size of $5 \times 6 \times 3.5\,m^3$.

2. MPCM manufacturing and cooling system design

During the microencapsulation process the polymer composing of encapsulating wall is induced to be separated as a new, viscous, polymer-rich phase in the ways of adding a non-solvent, lowering the temperature, changing pH, adding a second polymer, and changing other environmental condition. It is essential so that such changes would cause the polymer to come out of the solution and to aggregate around the core of droplet to form a encapsulating wall. This process includes the hardening of the coacervate layer, usually by a crosslinking agent. It is an absolute different process comparing with the conventional encapsulation process in which the wall is constructed first by mechanical process, and then the core material, PCM, is injected into prefabricated outer shell. For microencapsulation process, for its first stage, the core material is dispersed into solution, and then as a second stage, the outer surface wall is formed. The dispersing process of PCM is physically induced, but during encapsulation, a complicating physico-chemical processes are reacted. Through these processes, many reactions occur at interface and hence, can form microcapsules. In all such cases, capsule formation develops because monomers or oligomers reacting at an interface grow on a capsule shell. The shell forms a crosslinked or non-crosslinked polymer. There are many types of interfacial and in-situ encapsulation processes that have been reported in the patent literature.(7-10)

There are some parameters to be considered for the design of microcapsules as follows; (1) capsule size and distribution, (2) nature of core material (liquid vs. solid), (3) portion of core material that is acceptable, (4) nature of storage environment (time/condition), (5) how the capsule to be used. During the encapsulation process, the optical microscope should be frequently used to take a corrective action by detecting the presence/absence of wetting, evaluating capsule size and its geometry.

2.1 Material and instrument

Tetradecane as a core material, which has 5.8℃ in melting temperature (ACROSS in USA), was used. Melamin-Formaldehyde as its wall material was chosen. In this process, melamin reacts up to six formaldehyde molecules under slightly alkaline conditions to melamin methylol derivatives that contain six methylol groups per melamin molecules. When heated, the methylol-melamine is condensed to form a cross-linked structure. An acid compound can be added to accelerate the curing process. The melamin monomer was purchased from SAMSUNG CHEMICAL Co. The dispersing surfactant and its instrument were used from SMA (Styrene maleic anhydride copolymer, SOLUTIA in USA) and homomixer (ME100LC, ROSS in USA).

2.2 In situ encapsulation process

The first in-situ encapsulation process based upon formaldehyde polymerization chemistry is dissolved. The first step is to form a melamine-formaldehyde (MF) prepolymer. This is done by heating an aqueous MF mixture at pH 8~8.5 and 60℃ for 1 hr. The second step is to dilute and acidity the MF prepolymer solution. And finally the system is allowed to react and MF resin polymerizes to form a highly cross-linked MF shell around the dispersed droplets of core material.

2.2.1 Emulsification

Some amount of SMA was dissoved in over

90℃ to make 0.1~5 wt% solution, and then cooled down to atmospheric temperature. SMA solution was mixed with tetradecane and water for 7~12 minutes with homomixer. To be well stabilized the form of droplets, the speed of homomixer were regulated from 3,000 rpm to 10,000 rpm.

2.2.2 MF-prepolymer

The prepared melamin monomer, formaldehyde, and aqueous solution were dispersed in a reacting tank controlled by 60℃, and stirred for 10~20 minutes. Then, semi-transparent MF-prepolymer solution was obtained.

2.2.3 Encapsulation

A water-immiscible core material was emulsified into the acidified aqueous MF-prepolymer solution. The system at the temperature of 60℃ was stirred by 600 rpm over 3 hrs to react and MF resin polymerized to form a highly crosslinked MF shell around the dispersed droplets of core material.

2.3 Characteristic analysis and durability test

Their shapes and agglomeration of produced capsules were checked by a optical microscope (Olympus BX50), and size distribution was measured by a particle size analyzer (FRITSCH). To analyze the thermal properties of encapsulated particles differential scanning calorimeter (DSC550, Instrument Specialists, Inc.) was used. In order to apply micro-capsules for storing and transporting thermal energy there is a significant required characteristic of produced capsules, that is a durability which can keep their shapes with little breakage and without agglomeration. For the present study, a practical test for the durability of MPCM slurry was conducted by running three different operating types of pumps, which were centrifugal, peristaltic, and mono pumps. Figure 1 describes the definition of capsule breakage. The density of produced capsule was ranged within 870~910 kg/m^3, after circulation the unbroken capsules were floated, while shells (melamin) of broken particles were sunk due to their higher density, 1,570 kg/cm^3. Table 1 shows manufactures and models of three different types of pumps used for the present evaluation.

$$\text{Breakage fraction } BF_d = \frac{(L_0 - L_t)}{L_0} \times 100\,(\%)$$

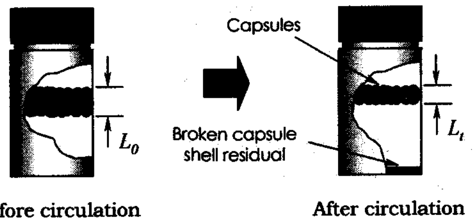


Fig. 1 Durability test for measuring particle breakage fraction.

2.4 Experiment of cooling system

A cooling system utilizing MPCM slurry as a thermal medium as well as working fluid was constructed as described in Fig. 2. The system was mainly consisted of storage tank of 1 m^3 capacity, which had contained eight PCM containers sized of 800×800×100 mm^3 each, a refrigerator of 2 RT (1 RT = 3,320 kcal/h), one fan coil unit, and etc. A container house of 5×5×3.6 m^3 was constructed for the present purpose.

Table 1 Pumps used in durability test

	A	B	C
Comp.	HANIL	MASTERFLex®	CHEON SEI
No.	PDB-40	L/S 7553-70	MONAS 3LB-08
Type	Centrifugal	Peristaltic	Mono

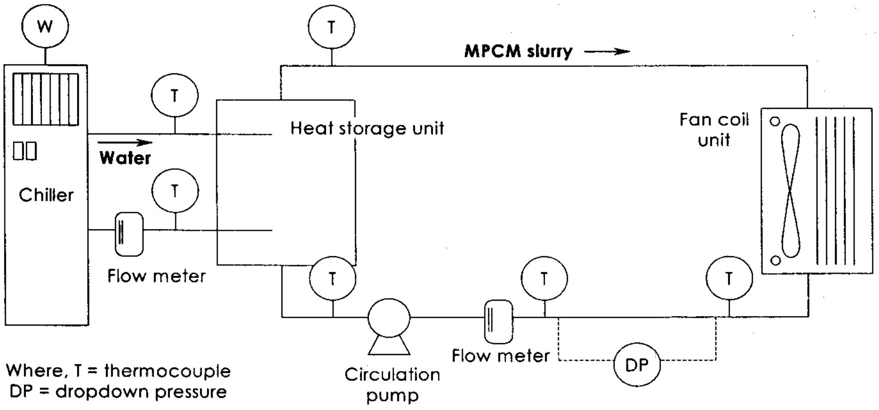


Fig. 2 Basic concept of circulating MPCM slurry as a room cooler.

To increase an efficiency of thermal storage tank, eight PCM containers, the total volume of 400 liters, which were filled with tetradecane, were arranged. The system was tested by varying 10 wt% and 20 wt% in the mixing ratio of MPCM slurry, and it was compared with water cooling system as thermal storage and working fluid. To use off-peak period for storing cooling energy the thermal cooling system was operated from 10 pm to 8 am in next morning. The room cooling test was lasted until the temperature of MPCM slurry/or water in the thermal storage tank was reached to 12℃.

During storing cold energy into the storage tank refrigerant from a refrigerator was circulated into coils passing through PCM containers. MCPM slurry was transported by centrifugal pump, which had a 8 m head, to a fan coil unit set up in the well-insulated container house. The capacity of pump for circulating refrigerant was regulated at 20 L/min. There were two flowmeters at the inlet and outlet of the thermal storage tank. And the pumping rate of MPCM slurry was automatically controled by the rpm of centrifugal pump, which was interfaced at the room temperature set-up at 18℃. As shown in Fig. 2, T-type thermocouples were installed to measure temperatures at several places such as both inlet and outlet of refrigerator, thermal storage tank, and fan coil unit. To reduce heat loss from the piping all flow lines were insulated.

3. Results and discussion

By adopting in-situ polymerization process, a high efficiency and mass production system for manufacturing MPCM slurry, which was encapsulated by melamin-formaldehyde with tetradecane as a core material, was designed and constructed. For the optimization of the process, various manufacturing conditions such as mixing ratio, surfactants, and temperature, etc., were tested and its reliability was also confirmed through repeated production test in order to obtain well-controled sizes and properties. As result of a well formed setting-up

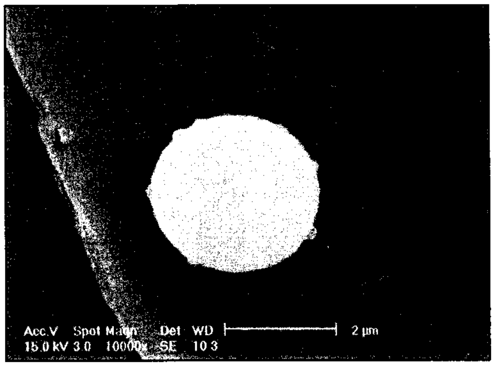


Fig. 3 SEM photograph of a MPCM.

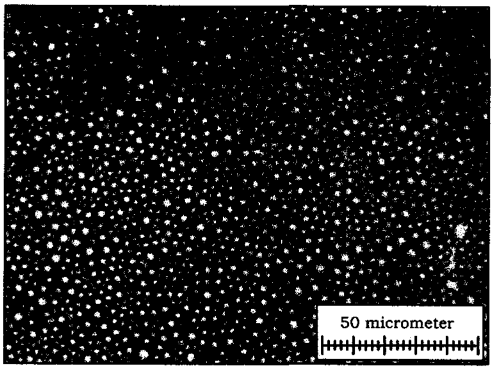


Fig. 4 MPCM slurry prepared by in-situ polymerization.

condition, a dried particle observed by SEM has shown in Fig. 3, and also Fig. 4 has shown MPCM slurry taken by the optical microscope. Figure 5 has described a result of DSC analysis, in which two peaks have appeared as the result of endothermic process. One is occurred at 9℃ for tetradecane and the other is placed at 380℃ for melamin. As a result of the analysis of particle size, the average diameter of produced capsules was found to be 5 μm as shown in Fig. 6. And also, the measured specific gravity of MPCM particles after drying by a spray dryer was ranged to 0.87~0.91 for which had resulted from 0.76 for the specific gravity of PCM as a core material and 1.57 for that of the shell. Therefore, it has been observed that the encapsulated particles in MPCM slurry diluted into water are clearly divided into two layers after the long period of time without disturbing the slurry as a result of different specific gravity of water and capsules. After circulating MPCM slurry through the system line, the remnant of skin of ruptured capsules, which is melamin-formaldehyde, has found to be settled down to the bottom due to higher specific gravity of shell material than tetradecane. The particles could be broken by both the shear stress of pump blade and the thermal shock after repeated volume change of phase change material.

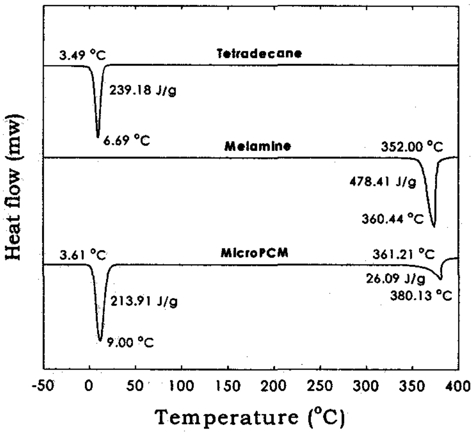


Fig. 5 DSC analysis for MicroPCM powders.

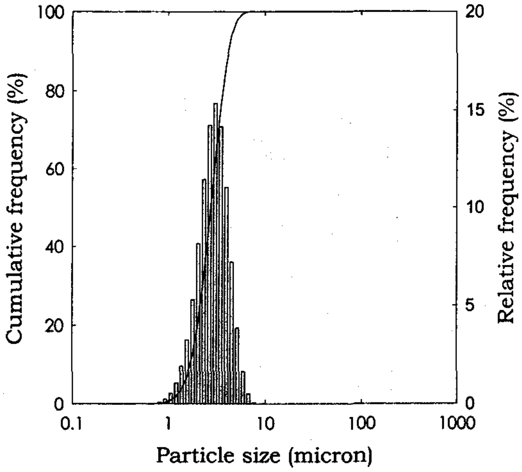
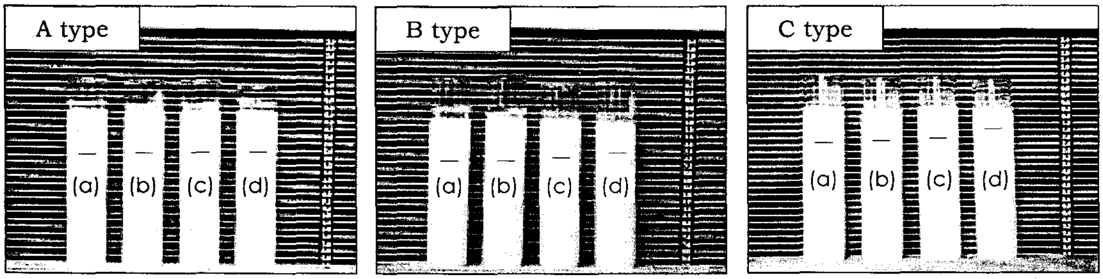


Fig. 6 Particle size distribution for produced MPCM particles.

In order to evaluate the durability of MPCM slurry, it has been diluted into 10 wt%. Figure 7 has shown the resulted MPCM slurry after circulating a system line with three different types of pumps for a certain period of time. As mentioned above, the durability of capsules can be evaluated with the breakage of capsules. As shown in Fig. 7, the layer of capsules floated at the top of the test cylinder has been reduced as the pumping cycle is increasing, while the broken shells of capsules are piled up at the bottom. For the durability test,

(a) 10 wt% PCM slurry (b) After 3,000 cycle (c) After 6,000 cycle (d) After 9,000 cycle



Centrifugal pump Peristaltic pump Mono pump

Fig. 7 Breakage fraction of MicroPCM after numbers of circulation with various pumps.

there was no heat exchange to MPCM slurry and the breakage of capsules has resulted from only the shear stress of pump during circulation.

It can be concluded that it has been little broken capsules if the thicker layer of floated capsules at the top is remained. As a result of Fig. 7, the centrifugal pump has been less capsule breaking than other types of pumps, peristaltic pump and mono pump. Especially, the mono pump, referred to type C, has been found to be the highest capsule broken rate due to the principle of the pump in which the screw type of both stator and rotor has rotating to feed MCPM slurry. As seen in Fig. 7, it has been clearly noted that the phase separation after centrifuge between PCM and capsules has been observed, which is caused by the broken capsules.

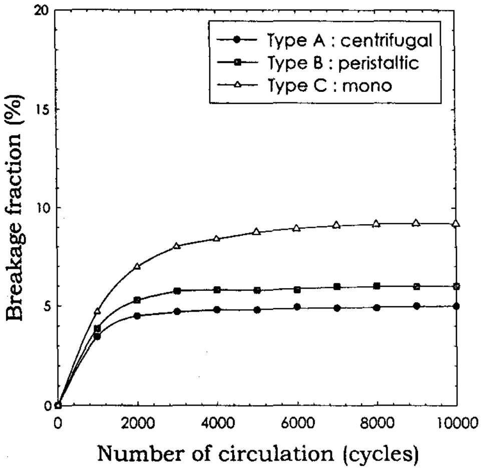


Fig. 8 Breakage fraction of microcapsules after circulation.

In order to investigate the effect of pump types on capsule breakage, as mentioned earlier, three different types of pumps were tested, that is, (a) centrifugal pump, (b) peristaltic pump, and (c) mono pump. It has been concluded that the centrifugal pump and peristaltic pump are relatively showing less breaking capsules than the mono pump. Figure 8 shows the breaking fraction of capsules, which is defined in Fig. 1, with respect to the pump type and circulation cycles. As described in Fig. 8, the mono pump has resulted as much as around 10% at 10,000 cycles, while the capsule breaking rate by both centrifugal pump and peristaltic pump are less than 6%.

Figure 9 shows the result of operation of cooling system in the model house with respect to 10 wt%, 20 wt%, and chilled water. During the experiment the room temperature was set to 18℃. As a result, it took 60 minutes to reach at the setting temperature after running with 20 wt% slurry, while by chilled water it took 2 hours. The working fluids, PCM slurry and chilled water, were cooled down to 3℃ to get low enough temperature to change the phase of the encapsulated PCM. As seen the top figure of Fig. 9, which is the result of temperature change of the working fluid, 20

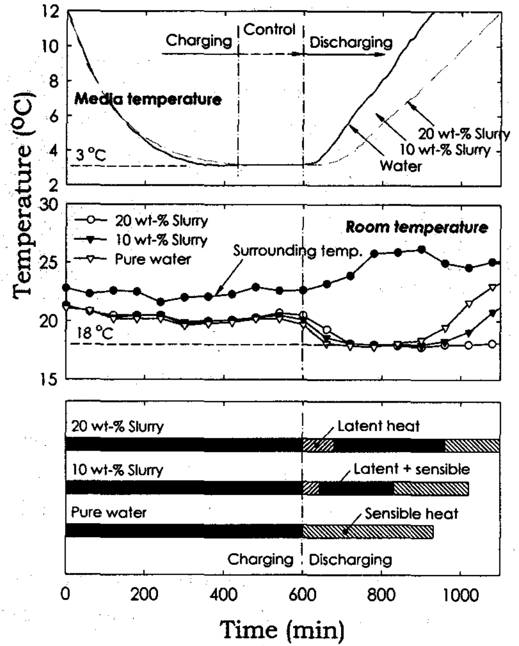


Fig. 9 Comparisons of performance between water and MPCM slurry as a coolant.

wt% MPCM slurry at 3℃ has been lasting 80 minutes longer than the chilled water. That is, it could be noted that PCM in capsules has released more heat as much as the time difference. For the present experiment, the cooling system was initiated at 10 am and the system was set to shut down automatically when the outlet temperature supplied by working fluid from the storage tank was reached to 12℃. As a result, the system was operated for 5.3 hours by the chilled water, while it was run for 10 hours with 20 wt% MPCM slurry. Conclusively, it has tested the possibility of a new working fluid which is pumping latent heat itself to the demand, and additionally the cooling system utilizing MPCM slurry may have the advantage of saving energy by adopting off-peak electrical power.

4. Conclusions

The process of in-situ polymerization was applied for manufacturing microencapsulated PCM particles whose core material was tetradecane and the melamin-formaldehyde as surface medium. As a result, it was found that the average size was observed to 5 μm, formed in a shape of sphere, and its phase change was measured around 6℃. For the durability of produced capsules, three different types of pumps were repeatedly tested over 10,000 cycles. It was confirmed that the breakage fraction was placed under 10% in all types of pumps.

In order to investigate the applicability of MPCM slurry for a room cooling system, 5×5×3.6 m^3 scaled room was built. The experiments were performed to characterize MPCM slurry by comparing with the chilled water. As a result, MCPM slurries with 10 and 20 wt% were found to be increasing the effective cooling time to 33% and 90%, respectively, compared with the chilled water. It was noted that the latent heat in MCPM slurry had significantly contributed to store and transfer its thermal energy.

It has concluded that the cooling system utilized by MPCM slurry has shown a better efficiency to the conventional chilled water cooling system. Furthermore, if off-peak load thermal storage system is adopted for the present system, it could be expected to improve its efficiency and energy saving.

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