

Anti-Tacking Properties of Zinc Stearate Emulsion for CMB Rubber Sheet Prepared by Heat Treatment Process

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Abstract: CMB (carbon master batch) or FMB (final master batch) rubber sheet, which is compounded and stacked as sheets during the rubber manufacturing process, may become indivisible due to adhesion between sheets over time. Therefore, in the actual rubber process, various organic/inorganic solid powders or liquid surfactants as anti-tacking agent are applied to the surface of the rubber sheet to solve these problems. In the present study, we prepared an emulsion using TEA-oleate (triethanolamine oleate) as the emulsifier of the zinc stearate powder, and examined its properties necessary to be used as the anti-tacking agent. In the sample preparing process of the emulsion, a heat treatment process was introduced to further refine the zinc stearate powder. Changes in the emulsion stability, adhesion characteristics and heat treatment effects on the prepared samples were analyzed through DSC (differential scanning calorimetry), UTM (universal testing machine), and TGA (thermogravimetric analysis).

Keywords: Rubber, CMB, Anti-tacking, Peel Strength, Zinc Stearate, Heat Treatment.

1. INTRODUCTION

In general, the manufacture of many rubber products is made largely by the 2-step process. In other words, the first step is to manufacture and store the CMB (Carbon Master Batch) as sheet form by compounding the mixture of raw rubbers and carbon black (CB), the filling agent, etc., using a Banbury mixer or Roll mixer. The stored CMB sheet, then, is re-mixed into the FMB (Final Master Batch) state, with additional sulfur cross-linking system, to be molded under the proper processing condition. Among these processes, CMB and FMB rubber sheets that are stacked onto the sheet by sheet may become indivisible during reuse due to the adhesion between sheets. Therefore, in the actual rubber manufacturing process, various organic/inorganic fine solid powders or liquid surfactants are applied to the sheet surface to solve such problems. Materials used for such particular purposes are also called anti-tacking agents [1, 2].

Mineral fine powders such as talc, bentonite, or zinc stearate which is a kind of metal salt of fatty acids, may often be applied directly on to the CMB/FMB rubber surfaces as the anti-tacking agents. Since these methods, however, can cause serious problems like workability or environmental pollution problem due to the scattering of the excessive dust, they are commonly used as liquid emulsion forms made by using surfactants [2].

On the other hand, since the specific gravities of the above solid powders used as the anti-tacking agents are usually higher than 1.0, the suspensions in which the anti-tacking solid powders are emulsified by surfactants in the water, can cause the problems like storage stability due to the solid precipitations as time goes by, resulting in difficulties in reusing. In addition, in actual use, there may be coating problems due to the difference in surface tension between the anti-tacking agents and the CMB rubber surfaces or de-foaming problems due to the formation of bubbles. Therefore, the key point is that the water-dispersed anti-tacking agent must have all the required properties as the anti-tacking agent, *i.e.*, the basic anti-tacking characteristics as well as the sedimentation stability, surface coating applicability, and de-foaming characteristics.

Inorganic solid powders, such as talc or bentonite, are most commonly used as anti-tacking agents, but due to their high solid contents in the dispersion, serious problems such as clogging of spray nozzles or solid sedimentation during storage were reported, and when the agents applied to the rubber surface is dried, some particulates of the agent can be remained on the surface of the final rubber products as the spots without being fully mixed into the bulk rubber, causing product defect [3-6].

Metallic salts of fatty acids, such as zinc stearate, magnesium stearate and calcium stearate, are also widely used as the materials for anti-tacking agents. Among them, in the case of zinc stearate having the lowest melting point, which is as low as 120 °C, when the rubber product is molded, it can be mixed completely into the rubber composition, resulting in

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clean surface of the product without discoloration or defect on the surface of the final molded rubber product, and so is most commonly used. However, the bulk density of ordinary industrial zinc stearate powder is about 1.1 g/cm^3 , so if emulsification process is not performed properly, the emulsion may cause problems such as poor workability or not having the desired anti-tacking properties owing to the solid sedimentation [2-4].

Meanwhile, esters of fatty acids are the type of surfactants made by esterification reaction of alcohols and fatty acids. They are used a lot in cosmetics and food products, but are also used as industrial emulsifying agents of anti-tacking solid powders. Among them, amine-derivative fatty acid esters such as TEA-oleate which is made by esterification of TEA and long alkyl chain oleic acid have very hydrophilic properties [7]. Particularly, TEA-oleate not only represents the anti-tacking characteristics itself, but also has an advantage of being easy to use because of room temperature liquid state, compared to TEA-stearate (triethanolamine stearate) which is a waxy solid state at room temperature due to the melting point of $45 \text{ }^\circ\text{C}$ [8-10].

In the present study, therefore, TEA-oleate was prepared through the esterification reaction of TEA with oleic acid. It was used as the surfactant of the industrially produced zinc stearate powder as well as anti-tacking agent. Anti-tacking emulsion samples were prepared by introducing a heat treatment process and investigated their properties required to be used as an anti-tacking agent. As the results, it was revealed that, by introducing the heat treatment process, not only can the anti-tacking performance be improved, but sedimentation stability also can be improved. Changes in the sedimentation stability and adhesion characteristics and heat treatment effects on the samples were analyzed through Differential Scanning Calorimetry (DSC), Universal Testing Machine (UTM), and Thermogravimetric Analysis (TGA).

2. EXPERIMENTAL

2.1. Materials

Zinc stearate powder of general purpose grade (Shin-Won Chemical, Korea), particle size of ca. $40 \mu\text{m}$, was purchased as the solid anti-tacking ingredient of the emulsion and was used without any additional refining process. TEA-oleate, as emulsifier, was prepared and used through the synthesis of TEA of

extra pure grade (Duck-San Chemical, Korea) and oleic acid (Duck-San Chemical, Korea, Extra Pure). An auxiliary surfactant was prepared by mixing two sorbitol-derivative surfactants, Tween-80 (polyoxyethylene 20 sorbitan monooleate) and Span-80 (sorbitan monooleate)(Duck-San Chemical, Korea). Chloroprene rubber based CMB rubber sheet with Shore-A hardness of 45 was supported from Yoonyoung Chemical (Korea) for the measurement of anti-tacking characteristics. Basic material properties for the sample preparation are shown in Table 1.

Table 1: Physical Properties of Materials for the Sample Preparation

Physical Property	TEA	Oleic Acid	Zinc Stearate
Density [g/mL]	1.124	0.895	1.095
Molecular weight [g/mol]	149.19	282.47	632.33
Melting point [$^\circ\text{C}$]	21.60	13~14	120~130
Solubility in water	miscible	insoluble	insoluble
Appearance	colorless liquid	yellowish oily liquid	white powder

2.2. Sample Preparation

2.2.1. Heat Treated Sample-1

8 g of TEA and 50 g of oleic acid were added to a 1000 mL beaker and heated on a hot plate up to $130 \text{ }^\circ\text{C}$ and stirred during 1hr at a speed of 500 rpm using a magnetic bar to complete the synthesis of TEA-oleate by esterification reaction. Then, 12 g of auxiliary surfactant, which is the mixture of Tween-80/Span-80, was added. Then 50 g of zinc stearate powder were put in slowly. Here the hydrophilic-lipophilic balance (HLB) value of the Tween-80/Span-80 mixture was quantified in advance to 11.5. Since HLB values of Tween-80 and Span-80 are 15 and 4.3, respectively, HLB value of the mixture can be calculated according to Eq. 1 [13].

$$\begin{aligned} \%(\text{A}) &= (\text{X} - \text{HLB}_\text{B}) / (\text{HLB}_\text{A} - \text{HLB}_\text{B}) \times 100 & \text{and} \\ \%(\text{B}) &= 100 - \%(\text{A}) & (1) \end{aligned}$$

Mixture of all ingredients was stirred for 30 min at 500 rpm at $130 \text{ }^\circ\text{C}$ finally to form a clear, pale yellowish liquid single phase.

Lastly, 600 g of $60 \text{ }^\circ\text{C}$ water was added slowly and stirred continuously to cool to room temperature. The

concentration of the final heat-treated sample-1 was 16.7 wt%. Formulation for the heat-treated sample-1 is shown in Table 2.

Table 2: Formulation for the Heat-Treated Sample-1

Component	Composition [g]
TEA	8
Oleic acid	50
Zinc stearate	50
Tween-80/Span-80 mixture	12
Water	600

2.2.2. Non-Treated Sample-2

For the non-treated sample-2, process of the synthesis of TEA-oleate and the addition of auxiliary surfactant was the same as in the preparation of sample-1. Then, the mixture was cooled to about 60 °C without further heat treatment.

Finally, 600 g of 60 °C water was added in first and then put 50g of zinc stearate powder in slowly and stirred continuously to cool to room temperature. The overall flow diagram for the sample preparation was shown in Figure 1.

2.3. Analysis of Characteristics

For the prepared sample-1 and sample-2, the following characteristics analysis was performed for the

diluted sample emulsions so that the total concentration of both samples was 2%.

2.3.1. Emulsion Stability

After filling the 100mL mass cylinder with each diluted sample emulsion at a predetermined level and leaving it for 72 hrs at room temperature, the level of phase-separated and precipitated zinc stearate powder was measured. In addition, a comparative analysis was conducted on how easily the solid sediments were transferred by pouring slowly the suspended solid.

2.3.2. Anti-Tacking Property

QM 100SE (QMESYS Co. Ltd.) universal testing machine (UTM) was used for analyzing the anti-tacking properties of samples. For the preparation of test specimens, two CMB rubber sheets of 50 mm (W) x 100 mm (L) x 8 mm (t) were heat-treated in advance by leaving them in a 100 °C oven for 30 min and immersed in the sample emulsion, then dried them again at 100 °C oven for 30 min. The two dried rubber sheets were placed against each other and squeezed for 30 min using the compression press so that the total thickness of the specimen was 8 mm. The final test specimens were prepared by cutting the squeezed rubber sheet to 40 mm (W) x 100 mm (L) and tested on UTM using the 90 ° T-Peel Test method to determine the peel strength.

2.3.3. Thermal Characteristics

DSC experiment was conducted using DSC-7 Differential Scanning Calorimeter (Perkin Elmer Inc.)

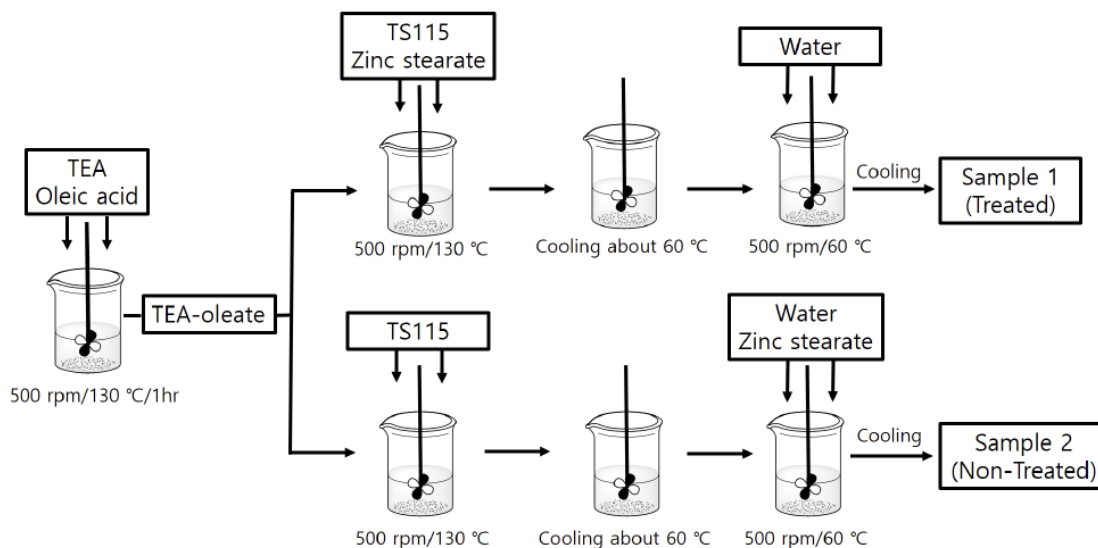


Figure 1: Schematic representation for the sample preparation.

Samples were prepared by completely drying the suspension in the 100 °C oven and taking about 10 mg of the obtained solid. A calorimetric change curve was obtained while raising the temperature from room temperature to 180 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

TGA experiment was performed using a TGS N-1000 (Scinco Co. Ltd.). Temperature change curve was obtained at a rate of 10 °C/min under a nitrogen atmosphere of 10 cc/min. As in DSC experiment, about 10 mg of the dried solid was used as the sample.

3. RESULTS AND DISCUSSION

3.1. Emulsion Stability

Figure 2 shows the sediment precipitated of sample suspensions for 72 hrs at room temperature when left in a vibration-free environment. As can be seen in Figure 2, although the phase separation did not occur as a whole, it was clearly confirmed that some precipitates were formed. In the case of heat-treated sample-1, it was confirmed that the sedimentation amount for the same time was remarkably smaller than non-treated sample-2. In addition, when the sediment was poured slowly to another vessel, it was confirmed that the sediment in sample-1 moved well while the sediment in sample-2 did not migrate well due to the particle agglomeration. It can be said that this phenomenon in the sample-1 exhibits it can easily be restored to the original suspension even with slight

stirring, which is a very important operational condition for the workers in the industry field.

3.2. Anti-Tacking Properties

Figure 3 is a graph showing the results of the measurement of the peel strength of the samples prepared with- and without- heat treatment. As can be seen from the figure, peel strength of the non-treated sample-2 was about 2.0 kg_f/mm while that of heat-treated sample-1 exhibited a significantly decreased value of about 0.5 kg_f/mm.

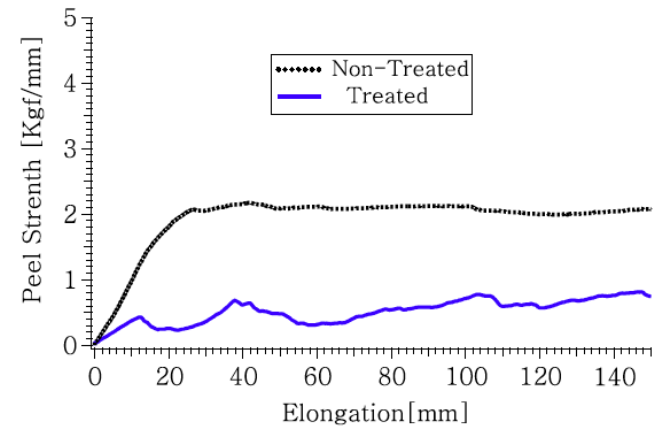


Figure 3: Peel strengths of heat-treated and non-treated samples.

In fact, in a domestic rubber-related factory, when the peel strength is measured using the same method as in this experiment, if the peel strength value

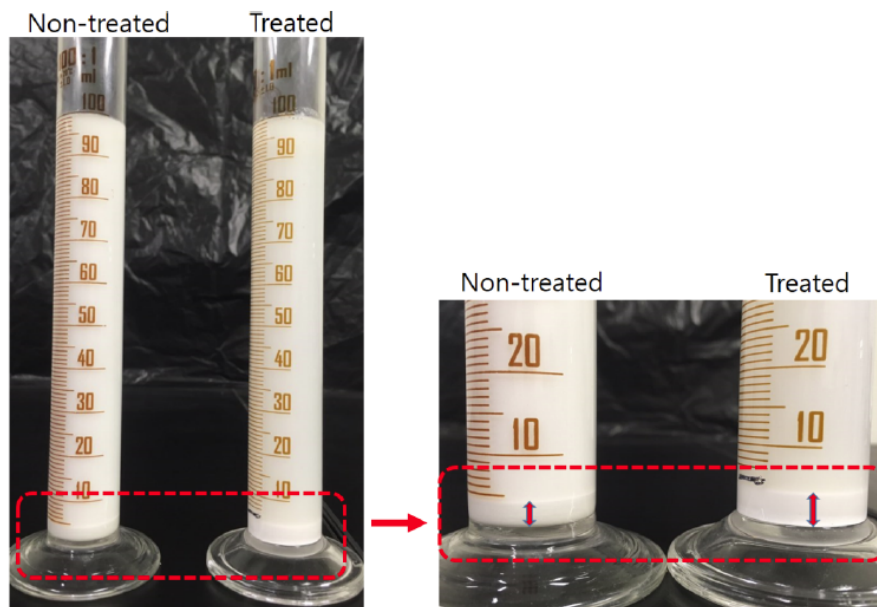


Figure 2: Solid sedimentation of the sample suspensions for 72 hrs at room temperature.

exceeds about 1.0 kg/mm, the anti-tacking characteristics are deemed insufficient for the practical uses in the factory work field. Therefore, when applying these criteria, the results of the present study can be thought to have a decisive effect on the anti-tacking characteristics, whether or not the heat treatment process is introduced in the manufacture of anti-tacking emulsion samples. In addition, the peel strength characteristics shown in this study can be said that the sample-1 has sufficient properties as an anti-tacking agent.

3.3. Thermal Properties

In general, zinc stearate, with two long alkyl chains of 18 carbons derived from stearic acid melts at a temperature range of 120 to 130 °C according to the production method. The crystal structure at room temperature is composed of a lamella type of trans-stranded alkyl chains. When melting, the alkyl chains are transformed into the amorphous liquid phase while retaining the co-ordination structure [11, 12].

Thermograms obtained by dynamic DSC measurement of two emulsion samples are shown in Figure 4. As can be seen in the figure, the overall melting curve of the heat-treated sample-1 shows relatively broader and smaller than that of the non-treated sample-2. From these results as also seen in Table 3, it can be seen that all of the melt-related temperatures such as initial melting temperature (T_{initial}), peak melting temperature (T_{peak}) and terminal melting temperature (T_{end}) are significantly low as compared with sample-2. Particularly, the melting enthalpy of the samples showed a great difference depending on the presence or absence of heat treatment, exhibiting 85.5 J/g and 134.9 J/g, respectively. It can be seen from these results that, when the molten zinc stearate is cooled below the melting temperature and is recrystallized to a layered crystal structure, a serious change in the size or structure of the crystal phase occurred. That is, since both TEA-oleate and the auxiliary surfactant (a mixture of Span-80 and Tween-80) have the long alkyl chain group having 18 carbons derived from oleic acid, a strong mutual chain interactions between these and the long alkyl chains of zinc stearate can be caused in the recrystallization process. In the present study, we no longer identified actual changes in particle size due to heat treatment or changes in crystal structures, but when considering the results of the sedimentation

experiment and the results of the peel strength test together, it is possible to consider that zinc stearate powder may be recrystallized as much smaller sizes or relatively less compact structures than the conventional powder due to the result of this mutual interactions and the stirring effect during cooling. From the viewpoint of practical applications, it can be said that the results show that, even if the same quantity of zinc stearate powder is emulsified as it is, the introduction of heat treatment process can lead to much more improved emulsion stability and anti-tacking performance.

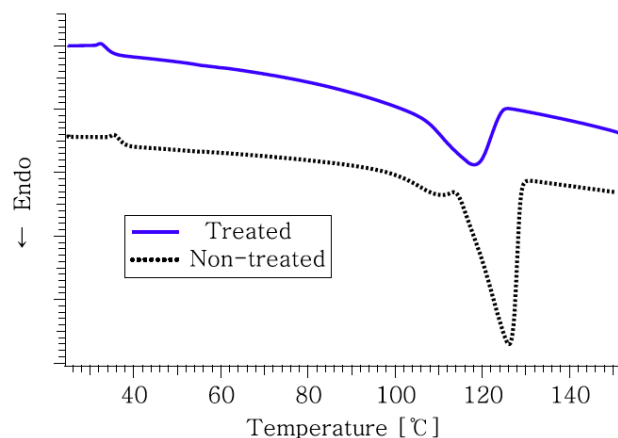


Figure 4: DSC thermograms of heat-treated and non-treated samples.

Table 3: DSC Results for Heat-Treated Sample-1 and Non-Treated Sample-2

Sample	Value			
	T_{initial} [°C]	T_{peak} [°C]	T_{end} [°C]	ΔH [J/g]
sample-1	70	117.8	124.3	85.5
sample-2	80	126.2	128.8	134.9

Meanwhile, the results of the TGA experiments were shown in Figure 5. As seen in the figure, the volatilization region of surfactant molecules in the range of 150 ~ 350 °C and the decomposition region of zinc stearate in the range of 350 ~ 450 °C can be confirmed. Thermal stability of heat treated sample-1 is relatively somewhat higher in the volatilization region, whereas the degradation region is not significantly different. On the other hand, TGA thermograms converted to DTG curves were shown in Figure 6 in order to examine the changing region more closely. As can be seen in the figure, in the case of the non-treated sample-2, the surfactant volatilizes continuously in the volatilization region as the temperature rises because

the surfactant has a relatively larger molecular weight distribution, showing the higher volatile peak at around 200 °C. On the other hand, in the case of the sample-1, the lower molecular weight surfactants in the original mixture may be separated out during the recrystallization process. It can be, therefore, considered that the volatilization is completed at a lower temperature than sample-2. In addition, the temperature at around 350 °C at which decomposition begins is somewhat higher in sample-1 than sample-2, which can be understood as a result of the strong mutual interactions between the long alkyl chains during recrystallization process as was considered above. These phenomena can be interpreted that the relatively low molecular weight molecules contained in the surfactants are more thermally stabilized in the heat treatment process, and may affect the micro-powdering during the recrystallization of the molten zinc stearate as shown in the DSC results.

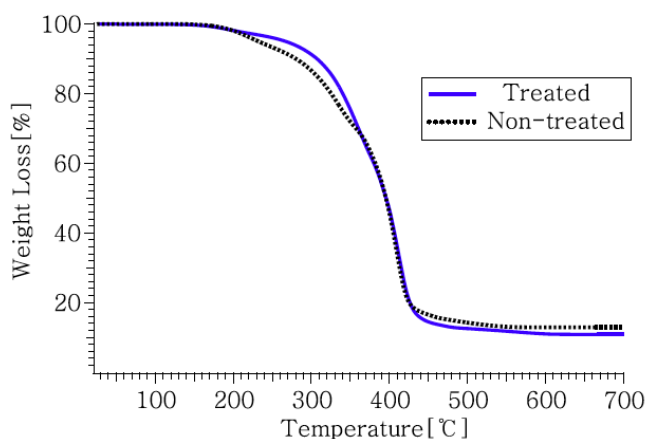


Figure 5: TGA thermograms of the heat-treated and non-treated samples.

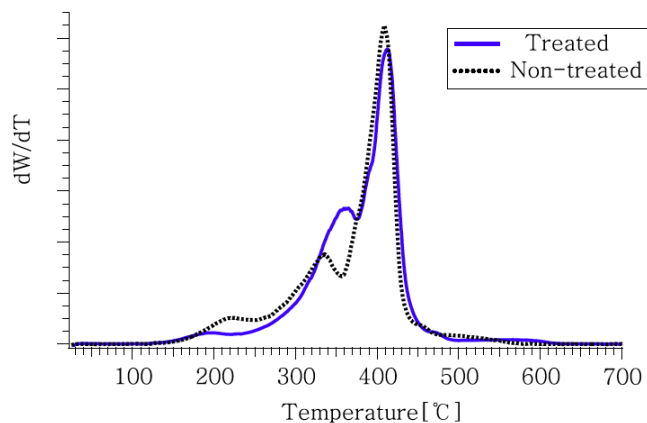


Figure 6: DTG thermograms of the heat-treated and non-treated samples converted from Figure 5.

4. CONCLUSION

A study on the preparation of stable aqueous suspension of industrial grade of zinc stearate powder using TEA-oleate as a main surfactant was performed. Heat treatment process was introduced into the sample preparation process. Emulsion stability of the samples was examined by measuring the sediments height. UTM was used to examine the anti-tacking characteristics. DSC and TGA were also utilized to investigate the effects of heat treatment on emulsion stability, anti-tacking characteristics and thermal properties.

In the case of the heat treated sample, the sedimentation stability of the emulsified suspension could be considerably improved by introducing heat treatment process. The peel strength value of the heat treated sample was remarkably decreased by 4 times or more than that of the non-treated sample. Initial melting temperature of zinc stearate of the heat-treated sample was decreased by about 10 °C than that of the non-treated sample. Particularly, the melting enthalpy of the heat-treated sample was greatly reduced compared to the non-treated sample, changing from 134.9 J/g to 85.5 J/g. In the recrystallization process of zinc stearate by heat treatment, it was thought that, by the strong interactions between the long alkyl chains of surfactants and those of molten zinc stearate and the stirring effect during cooling, zinc stearate powder may be recrystallized as much smaller sizes or relatively less compact structures than the original powder.

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