pyrolyzates having the same average chain lengths. A few products prepared at 200 °C contained more highly condensed phosphates than any pyrolyzate prepared from urea phosphate under the same conditions of time and temperature, but no long-chain crystalline ammonium polyphosphate was found. Most of these pyrolyzates contained some trimetaphosphate, a ring compound, and the pyrolyzate prepared at 200 °C from the high-urea mixture contained 45% of its phosphate as the trimetaphosphate.

Solubility. A detailed study of the solubility of urea phosphate pyrolyzates was not made, but a few general observations can be reported. Biuret is the first compound to crystallize with increasing concentration of pyrolyzate solutions, and urea usually is the next compound to crystallize, especially at the lower average chain lengths. The ammonium polyphosphates produced by pyrolysis are at least as soluble as those produced by conventional means. No metallic phosphates precipitated from pyrolyzate solutions containing 10% of the impurities in wet-process phosphoric acid. Therefore, the maximun concentration of clear solution fertilizers was limited primarily by the biuret content.

SUMMARY

In conclusion, several points should be emphasized. The pyrolysis of urea phosphate is rapid at temperatures above 126 °C. Most of the condensation of polyphosphate occurs during the first 1 to 2 min when the pyrolysis is exothermic. The addition of anhydrous ammonia enhances the reaction rate initially but later retards it. All water of condensation is released by means of urea hydrolysis and no free water is expelled. The distribution of phosphate species in the pyrolyzates is similar to but not the same as that in superphosphoric acid.

Small amounts of biuret are formed as a by-product. The biuret increases with increase in the average chain length of the phosphate, reaches a maxima at average chain length of 2.7, and then decreases with further increase in the chain length. It increases with increasing urea in the product and decreases with increasing ammonia content. Pyrolysis of mixtures of urea phosphate and monoammonium phosphate gives products containing less biuret, but the rate of pyrolysis is decreased. The precipitation of biuret limits the grade of clear solution fertilizers that can be made from urea phosphate pyrolyzates.

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Heat Degradation of Carrageenan in a Milk Salt System

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A hydrolytic effect of heat sterilization on carrageenan (Seakem 2) was demonstrated in a synthetic milk salt system. The heat-induced changes in carrageenan included increased electrophoretic mobility on cellulose acetate and agarose, reduced viscosity, increased reducing power, and reduced molecular weight by sedimentation equilibrium centrifugation. The apparent weight average molecular weight decreased by 42% after 20 min of heat treatment at 122 °C. The hydrolytic process was a first-order random degradation with a velocity constant at 122 °C approximately twice as large as has been reported for heat degradation of carrageenan in aqueous solution at pH 7.0. The increased hydrolysis in the milk salt environment was attributed to a drop in pH which occurred during heating of that system which was greater than for normal milk. The ultracentrifuge analysis revealed that sodium carrageenate in 0.05 M sodium cacodylate buffer (pH 7) containing 0.25 M sodium chloride at 35 °C undergoes a reversible, pressure-dependent dissociation. At 20000g species were produced with weight-average molecular weights of 8.5×10^4 for unheated samples and 5.1×10^4 daltons for samples previously heated in a milk salt system at 122 °C for 15 min. Extrapolation to zero speed indicated a molecular weight of 2.3×10^5 for the undissociated, unheated carrageenan aggregate.

Carrageenan is used as a stabilizer in a number of manufactured milk products, including evaporated milk and sterilized infant milk formulas. The mechanism by which the products are stabilized is still not well understood, but appears dependent upon the protein reactivity and polymer size of carrageenan (Snoeren et al., 1975).

The heat degradation of carrageenan in aqueous solution has been studied by Masson (1955), Masson and Caines

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Table I. Composition of Milk Salt Solution[a] (pH 6.7)

Cations, mM/L		Anions, mM/L	
Na	18.2	P	11.6
K	39.4	Cl	32.4
Ca	9.0	SO_4	1.0
Mg	3.2	CO_2	2.2
		Citrate	9.6

[a] Jenness and Koops (1962).

(1954), and Masson et al. (1955), who followed the heat-induced changes in viscosity and reducing properties of an extract of the relatively low number average molecular weight ($\bar{M}_n$) of 75 500 daltons. These authors have reported an initial rapid degradation representing only about 0.3% of the complete hydrolysis, followed by a first-order random degradation with high velocity constants, indicating that carrageenan is heat labile. However, intrinsic viscosity measurements have shown that carrageenan in dilute solutions of low ionic strength is rigidly extended and consequently may respond to heat treatment in a different manner than when it is heated in the presence of electrolytes where it is more randomly coiled.

In a previous report (Hansen and Renoll, 1974), it was shown that when carrageenan is subjected to sterilization temperatures in a milk salt system, there is a heat-induced change of the hydrocolloid measurable by zonal electrophoresis and resembling acid hydrolysis. This change was accelerated by lowering the pH of the system. This present study was undertaken to further examine the effect of heat exposure of carrageenan in a milk salt environment.

EXPERIMENTAL SECTION

A milk salt solution (J & K) simulating milk ultrafiltrate was prepared according to Jenness and Koops (1962) as shown in Table I. The commercial carrageenan, Seakem 2 (Marine Colloids, Inc., Springfield, N.J.), was dispersed in the J & K solution at 0.5% concentration. The carrageenan solution was placed in 10-mL ampules which were heat-sealed. The filled ampules were heated for 0–20 min in an oil bath maintained at 122 ± 0.5 °C and then immediately cooled in ice water.

Viscosity Measurements. The viscosity of carrageenan solutions was measured using a No. 150 Cannon-Fenske capillary viscometer. The constant for the viscometer was determined by using Cannon-Fenske viscosity standards. The viscometer was allowed to equilibrate at 20 °C and a sample of 7 mL was utilized for the determination. The reported values are the average of three different readings.

Reducing Sugar Determination. The procedure by Nelson (1944) was used to determine the reducing sugar capacity of carrageenan at a wavelength of 660 nm and using a standard curve developed with galactose (r = +0.99). The number average molecular weight ($\bar{M}_n$) of carrageenan was determined based on the reducing power of the polysaccharide expressed in percent galactose. The following relationship was used for this determination:

$$\bar{M}_n = \frac{18\,000}{\text{galactose equivalent (\%)}}$$

Ferricyanide Reducing Value. The procedure by Crowe et al. (1948) for milk was followed, using a sample size of 10 mg of carrageenan contained in 2 mL of J & K solution and expressing the reducing value in absorbance units.

Cellulose Acetate Electrophoresis. Since acidic electrolytes have been used previously during the identification of carrageenan by zonal electrophoresis (Hansen and Renoll, 1974), a neutral electrolyte system was developed to avoid such acidic conditions that may endanger the validity of the electrophoresis. The electrolyte system was made by dissolving 12.15 g of trichloroacetic acid (TCA) in 1 L of water (0.075 M). Following pH adjustment to 7.0 with solid $Ca(OH)_2$, 150 mL of ethanol was added. The reagent was stable for at least a week when stored cold. The details of the procedure for electrophoresis have been reported previously (Hansen and Renoll, 1974). Prior to zonal electrophoresis, the heat treated carrageenan samples were pretreated with about 15 mg/mL of Amberlite CG-120 (Rohm and Haas), a cation-exchange resin in the sodium form, to remove the effect of gelling cations.

Agarose Gel Electrophoresis. Agarose electrophoresis was conducted on agarose plates purchased from Bioware, Inc., Wichita, Kans. The procedure by Stanley and Renn (1974) was followed except that the buffer was the same Ca-TCA–ethanol system used in cellulose acetate electrophoresis.

Ultracentrifuge Analysis. The molecular weight of carrageenan was obtained by sedimentation equilibrium ultracentrifugation using a Spinco Model E analytical ultracentrifuge equipped with Raleigh interference optics. The experiments were carried out at 35 °C using an AN-J rotor at 10 000 rpm until equilibrium (48 h). All samples were dialyzed to equilibrium against 0.05 M sodium cacodylate buffer (pH 7) containing 0.25 M NaCl (density: 1.015 g/mL at 35 °C). A Paar precision digital densitometer was used to obtain the value of 0.52 mL/g for the partial specific volume of carrageenan. Measurement of fringes was accomplished by using a Nikon profile projector, and the data were treated as high-speed meniscus depletion for obtaining the apparent weight average molecular weights ($\bar{M}_w$).

RESULTS

Heating carrageenan in the milk salt system caused an increase in the reducing power accompanied by a gradual drop in pH from 6.7 to 5.5 (Table II). The change in pH was in part due to changes in the J & K solution alone since the pH of the carrageenan–water system, subjected to the same sterilization conditions, was less drastic. The formation of reducing sugars as measured by the Nelson test is an indication of a beginning heat-induced hydrolysis of the carrageenan. The comparatively high ferricyanide reducing values show that other reducing substances may also have been generated prior to and during heating, possibly from sugar degradation. O'Neill (1955) has pointed out that the 3.6-anhydrogalactose units would be expected to break upon heat treatment, yielding hydroxymethylfurfural (HMF) and formic acid. The amount of HMF formed has been reported to increase when

Table II. Effect of Heat Treatment (122 °C) on Carrageenan in J & K Milk Salt Solution

Time, min	pH of heated carrageenan in J & K solution	pH of J & K solution	pH of carrageenan in water	Nelson test (galactose %)	Ferricyanide reducing value (absorbance units)
0	6.70	6.70	9.1	0.15	0.415
5	5.70	5.75	8.7	0.18	0.460
10	5.60	5.55	8.6	0.20	0.505
15	5.55	5.50	8.5	0.22	0.550
20	5.50	5.38	8.3	0.32	0.590

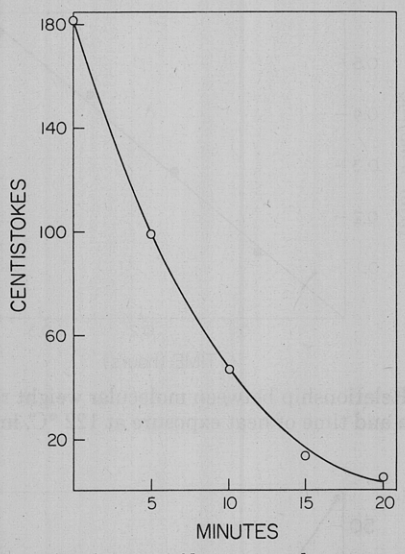

Figure 1. Viscosity changes of heat-treated carrageenan in a milk salt system.

heating carrageenan in an unbuffered solution in the presence of air on account of a decrease in pH which accelerates the formation of these compounds (Masson et al., 1955). The increase of the ferricyanide reducing value of carrageenan after heat treatment attests to the formation of reductones such as HMF and formic acid.

Figure 1 shows that a rapid decrease occurred in the viscosity of the carrageenan solution upon heating. The largest drop occurred during the first 5 min of the heat treatment.

Figure 2 shows the cellulose acetate electrophoresis patterns of the carrageenan samples. The pattern of untreated Seakem 2 is represented in this electrolyte system by a stationary zone and two migrating bands. The leading band has been identified as unaggregated κ-carrageenan and the slower as λ- or θ- (alkali-modified λ) carrageenan while the stationary zone is a result of aggregation of κ-carrageenan in the presence of calcium ions. The heat-treated samples showed a loss of the stationary zone, indicating a diminished ability of the κ-carrageenan to aggregate. There was also a reduction of the intensity of the leading band upon heating and an increase in the mobilities of the two migrating zones. These changes are the same as previously noted (Hansen and Renoll, 1974) for zonal electrophoresis in malonate buffer and which were attributed to hydrolysis.

Table III. Apparent Molecular Weights of Heat-Treated Carrageenan by Ultracentrifuge Analysis and Reducing Sugar Test

Heating time at 122 °C, min	Ultracentrifuge analysis		Reducing sugar test, $\bar{M}_n$
	Apparent $\bar{M}_w$	Correlat. coeff.[a]	
0	132000	+0.946	120000
5	113000	+0.986	100000
10	96000	+0.997	90000
15	83000	+0.988	82000
20	76000	+0.999	56000

[a] Linear correlation coefficient of the plot of ln concentration (fringes) vs. squared radial position.

The agarose gel electrophoresis results shown in Figure 3 demonstrated a decrease in intensity of the stationary zone of carrageenan upon heating. The breakdown of carrageenan is evidenced by the stronger moving front which represents low molecular weight fractions developed upon heat treatment and which enter the gel easily.

Quantitative information on polymer breakdown was obtained from the apparent weight average molecular weights ($\bar{M}_w$) determined by equilibrium ultracentrifugation and from the number average molecular weights ($\bar{M}_n$) calculated from the reducing-end groups determined by the Nelson test (Table III). According to these measurements, the polymer size of carrageenan decreased by 42% ($\bar{M}_w$) and by 53% ($\bar{M}_n$) after 20 min of heating at 122 °C.

The molecular weights for undegraded carrageenan listed in Table III are lower than the $\bar{M}_n$ value of 1.84×10^5 ascribed to this commercial product (Seakem 2) by the manufacturer (Marine Colloids, 1972). We have determined an uncertainty of mol wt ±4200 (standard deviation) associated with our ultracentrifuge measurements, which is much less than this apparent discrepancy. Possible abnormal results in the analysis due to charge effects or gelation can presumably be ruled out in this study because the conditions chosen for the ultracentrifugation would minimize or eliminate these effects.

We have further examined the conditions for the ultracentrifuge analysis and have concluded that the lack of ideal sedimentation behavior for carrageenan is the result of a reversible, pressure-dependent dissociation of a carrageenan polymer which is evident when the rotor speed is increased (Figure 4). The ultracentrifuge values in Table III are the apparent $\bar{M}_w$ at 10000 rpm which

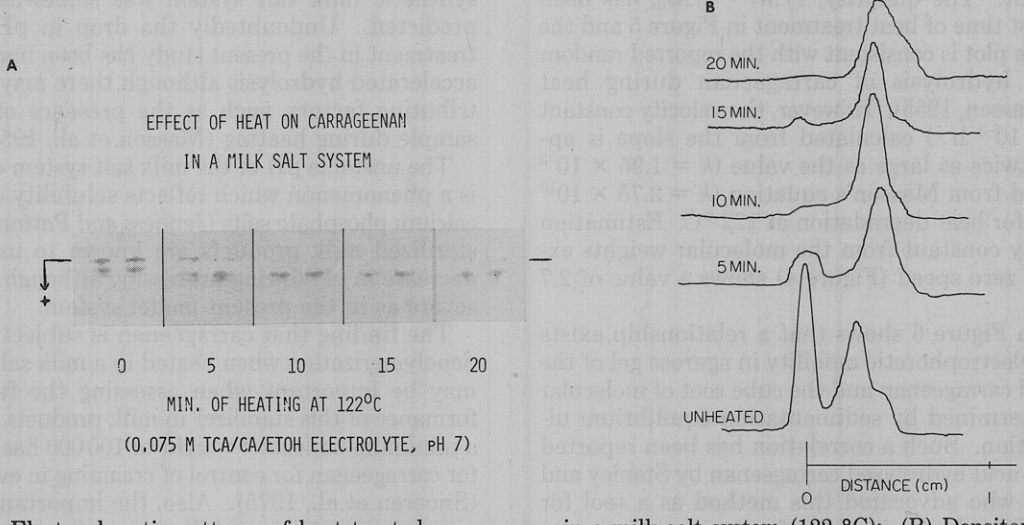

Figure 2. (A) Electrophoretic patterns of heat treated carrageenan in a milk salt system (122 °C); (B) Densitometer tracings.

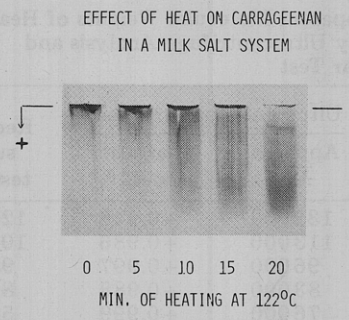

Figure 3. Agarose gel electrophoresis of carrageenan in a milk salt system.

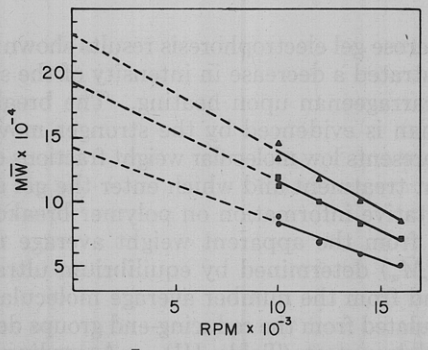

Figure 4. Variation in $\bar{M}_w$ of carrageenan at different rotor speeds at 35 °C: (▲——▲) unheated; (■——■) 5 min, 122 °C; (●——●) 15 min, 122 °C; Samples were dispersed and heated in the milk salt system, then dialyzed to equilibrium against the cacodylate/NaCl buffer.

therefore represent lower values than would be obtained for the same system in a nonstressed state. The highest speed attainable in our analysis was 16 000 rpm, corresponding to approximately 20 000g, which produced $\bar{M}_w$ values of 8.5×10^4 decreasing to 5.1×10^4 after heat treatment at 122 °C for 15 min in the milk salt system.

To study the kinetics of the heat hydrolysis, the following equation used by Masson (1955) and by Mark and Tobolsky (1950) for a first-order random degradation was applied to the ultracentrifuge data in Table III:

$$\frac{1}{M_t} - \frac{1}{M_0} = \frac{kt}{m}$$

where M_0 and M_t are the molecular weights at zero time and time t, respectively, m is the molecular weight of the monomer (250) as used by Masson (1955), and k the velocity constant. The quantity, $1/M_t - 1/M_0$, has been plotted against time of heat treatment in Figure 5 and the linearity of the plot is consistent with the reported random character of hydrolysis of carrageenan during heat treatment (Masson, 1955). However, the velocity constant ($k = 4.35 \times 10^{-3}$ h^{-1}) calculated from the slope is approximately twice as large as the value ($k = 1.95 \times 10^{-3}$ h^{-1}) calculated from Masson's equation ($k = 2.75 \times 10^{13}$ $e^{-29200/RT}$ h^{-1}) for heat degradation at 122 °C. Estimation of the velocity constant from the molecular weights extrapolated to zero speed (Figure 4) shows a value of 2.7 $\times 10^{-3}$ h^{-1}).

The plot in Figure 6 shows that a relationship exists between the electrophoretic mobility in agarose gel of the heat degraded carrageenan and the cube root of molecular weight as determined by sedimentation equilibrium ultracentrifugation. Such a correlation has been reported previously for acid hydrolyzed carrageenan by Stanley and Renn (1974), who advocated this method as a tool for molecular weight determination of carrageenan.

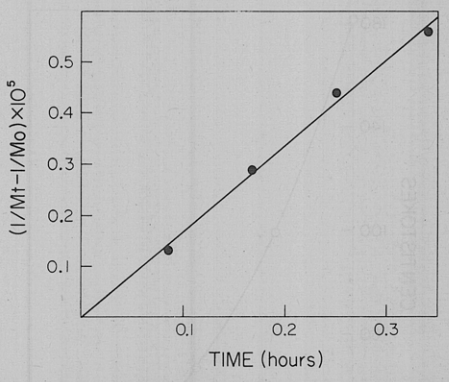

Figure 5. Relationship between molecular weight reduction of carrageenan and time of heat exposure at 122 °C, in a milk salt system.

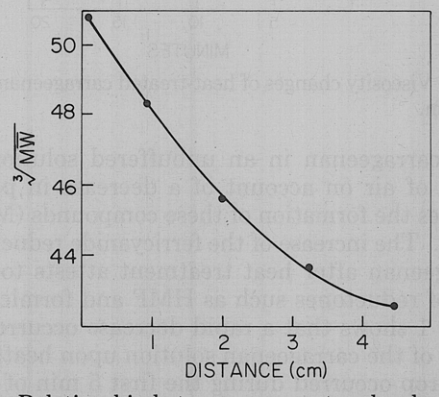

Figure 6. Relationship between apparent molecular weight of heat-treated carrageenan (122 °C) and electrophoretic migration in agarose gel.

DISCUSSION

The results of this study have shown that carrageenan in a synthetic milk salt system is affected by heat sterilization and confirm the findings by Masson (1955) that this colloid is heat labile. Electrophoresis on cellulose acetate strips and agarose gel showed changes in the electrophoretic behavior of carrageenan upon heating. The increase in the reducing power of carrageenan and the reduction in molecular weight, as determined by ultracentrifuge analysis, were consistent with hydrolysis attacking random points of the polysaccharide chain. Degradation as measured by agarose electrophoresis agreed with the ultracentrifuge data.

The velocity constant for the depolymerization in the synthetic milk salt system was somewhat larger than predicted. Undoubtedly the drop in pH during heat treatment in the present study has been important for the accelerated hydrolysis although there may be other contributing factors, such as the presence of air with the sample during heating (Masson et al., 1955).

The unstable pH of the milk salt system during heating is a phenomenon which reflects solubility changes in the calcium phosphate salts (Jenness and Patton, 1959). Batch sterilized milk products are known to undergo such a decrease in pH during processing although usually not as severe as in the present model system.

The finding that carrageenan is subject to significant depolymerization when heated in a milk salt environment may be important when assessing the functional performance of this stabilizer in milk products. For example, a minimum molecular weight of 100 000 has been reported for carrageenan for control of creaming in evaporated milk (Snoeren et al., 1975). Also, the importance of polymer size in respect to stabilization of α_s-casein has been

demonstrated with degraded carrageenan (Lin and Hansen, 1970) and has been shown to be associated with a limited range of molecular weight of the carrageenans from 100 000 to 300 000 (Lin, 1971).

We made the observation in this study that carrageenan is subject to a reversible, pressure-dependent dissociation similar to the effect observed for myosin by Josephs and Harrington (1967). Because of this effect, the apparent $\bar{M}_w$ determined by ultracentrifugation would appear to be lower than would be the case for measurements obtained without generation of pressure. Extrapolation to zero speed of the plot in Figure 4 indicates a $\bar{M}_w$ for the undissociated, unheated carrageenan (Seakem 2) of 2.3×10^5.

The number-average molecular weights ($\bar{M}_n$) for several commercial carrageenan types, calculated from intrinsic viscosity data, range from 1.02×10^5 to 2.20×10^5 (Marine Colloids, 1972). Snoeren (1976) obtained by light scattering a value of 7.18×10^5 ($\bar{M}_w$) for the commercial product Genulacta P100 (Kobenhavns Pektinfabrik, Denmark). Smith et al. (1957) estimated the molecular weight of a mixture of high viscosity commercial carrageenans from sedimentation coefficients and intrinsic viscosity data and reported 2.3×10^5 and 3.6×10^5 depending upon the method of relating these parameters. Goring and Young (1955) obtained the value of 12×10^5 ($\bar{M}_w$) for a laboratory sample of unfractionated carrageenan also from sedimentation coefficients and intrinsic viscosity data.

Large variations in the estimates for carrageenan polymer size may be expected because of the heterogeneity of unfractionated carrageenan extracts and because of differences in methods of extraction when heat is involved. However, our observation that carrageenan is an aggregated system which undergoes a pressure-dependent dissociation emphasizes the need to account for this effect when different methods are used in the assessment of the polymer size. Our results show the monomer $\bar{M}_w$ of Seakem 2 carrageenan to be less than 1.0×10^5 and decreasing when heated in a milk salt system.

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Effects of Dehulling on Tannin Content, Protein Distribution, and Quality of High and Low Tannin Sorghum

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High and low tannin varieties of sorghum grain were subjected to sequential dehulling operations to attempt to remove tannins. Up to 37% of the grains were removed in these procedures. Dehulling resulted in considerable (up to 45%) loss in protein content as well as in the removal of most of the tannins (up to 98%). Amino acid analysis of the dehulled grains showed a progressive decrease in the content of lysine, histidine, and arginine. The solubility distribution pattern of proteins from both varieties at various stages of dehulling showed marked differences. Using the low tannin variety as control, these observations were utilized in assessing the effect of tannins on the solubility characteristics of sorghum proteins. The observed differences are consistent with strong interactions between tannins and the kafirin (prolamin) protein fractions in sorghum.

Sorghum constitutes a major proportion of the world food grain production and is the third largest crop in the United States. A major drawback of sorghum as a food source is the high levels of polyphenols (tannins) associated with certain varieties of sorghum grain. Grain producers and breeders maintain high tannin varieties for their resistance to bird damage, favorable storage quality, desirable weathering, and resistance to preharvest germination. However, the low nutritional quality of high tannin

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