

Design, Rheology and Physicochemical Characterizations of Oil-in-water Emulsions Stabilized by Waxy Starch Derivatives

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Abstract: Simple emulsions (o/w) stabilized by octenyl succinic anhydrous (OSA) starch were studied. They were characterized by the evaluation of the rheological and physicochemical properties and, the observation under the light microscope in combination with granulometric analysis after formulation. The obtained results demonstrated the effects of the amount of OSA starch on the variation of the diameter of particles, stability of emulsions and their rheological behavior. The best characteristics were found in the emulsion with a ratio 40/60 (o/w) at high OSA starch concentration, because the substitution of the oil phase by the network created by the chains of the modified polysaccharides which could be the major factor in stabilisation of emulsions.

Keywords: Emulsion; OSA starch; Gelification; Rheology; Stability.

1. Introduction

The trend in the food industry is the searching for new natural products, biodegradable and beneficial for health. They are generally utilized in food formulations to replace fats while retaining the same original properties of the products obtained [1,2]. Modified polysaccharides are examples of natural stabilizers and emulsifiers due to their surface and gelling properties [3].

Among the polysaccharides, starch is abundant in nature; its chemical modification by the octenyl succinic anhydride (OSA) leads to starch derivatives with interesting characteristics that can be employed in food, cosmetics and pharmaceutical [4-6].

The substitution of the hydroxyl moiety of surface glucose monomers by OSA group disorders the granular structure of starch and decreases the solubility, pasting temperature and gelling capacity; while the water retention and cold storage stabilities are generally improved [7-9]. The degree of substitution (DS) is limited by the FDA to be less than 0.02 for food products. This parameter depends on many factors of reaction modification like temperature, pH, time and OSA concentration [10,11].

The introduction of the hydrophobic group OSA in the hydrophilic structure of starch gives an amphiphilic character to OSA starch. Due to its surface properties, this modified biopolymer is widely used in stabilisation of dispersed systems; it decreases the interfacial tension between the aqueous and oily phases and then forms an oil-in-water (o/w) emulsion by both electrostatic and steric mechanisms [12,13]. OSA starch concentration and the oil content are the major factors which describe the rheological behavior and the variation of the diameter of droplets [3,14]. These characteristics can be improved by adding another polysaccharide like xanthan gum as thickener to avoid creaming, flocculation and coalescence by the constitution of a droplet network [15,16]. The same effects were noticed when adding maltose or sucrose monoesters by increasing the emulsion viscoelasticity [17].

Low-fat products show interesting properties when OSA starch is used as fat replacer, keeping the same rheological parameters and texture [18,19]. While the texture of cookies made with OSA starch shows higher dough strength and lower cookie spread in comparison with normal ones [20]. In addition, the imitation of cheese products provides a reduced cost, calories and cholesterol since the animal fat is substituted by vegetable fat and proteins. For some cheeses, caseinate has been replaced by OSA starch [21]. This modified starch was also used to produce anti-oxidative microcapsules by electrostatic interactions with proteins and/or polysaccharides [22,23].

In this work, we focused on the formulation and physicochemical characterization of simple oil-in-water emulsions stabilized by OSA starch, and the evaluation of the influence of its concentration on the stability and distribution of the mean diameter of the dispersed particles.

2. Material and methods

2.1 Chemicals

OSA starch was supplied by REDA® (Representative of National Starch in Algeria). The oil phase is Sunflower oil purchased from a local supermarket; other chemicals of analytical grade were purchased from FLuka (Buchs, Switzerland).

2.2 Preparation of emulsions

The aqueous solution was prepared at different concentrations by dispersing well known amounts of OSA starch in distilled water. The oil phase was mixed with the aqueous phase at different ratios (30-70%), and homogenized using an ultra-Turrax homogenizer (IKA T25, Germany) for 10 min at 10,000 rpm and, at ambient temperature. The compositions of the formulated emulsions are mentioned in Table 1.

Table 1. Compositions of emulsions

Formulation	Oil phase ((%, in wt.)	Water (% , in wt.)	OSA starch (% , in wt.)
F01	70	25	5
F02	70	20	10
F03	60	35	5
F04	60	30	10
F05	50	45	5
F06	50	40	10
F07	40	55	5
F08	40	50	10

2.3 Microscopy and droplet size distribution

Optical micrographs of the stained emulsions, by 2% iodine solution, were captured using a micro Austria optical microscope equipped with a digital camera (Lumenera Infinity lite). The size of droplets was evaluated by the treatment of images using the ImageJ.Ink software.

2.4 Rheological measurements

The rheological behaviour of liquid emulsions was evaluated using an Anton Paar rheometer (MCR 302, Germany) equipped with a plate-plate system (diameter of 25 mm and a gap of 1 mm) at 20 °C. For the flow sweep experiments, the shear rate was ranged from 0.001 to 1000 s⁻¹. In order to determine the linear viscoelastic region, oscillation strain sweep experiment was realized in the oscillation strain ranging from 0.01 to 100% (frequency of 1 Hz and temperature of 20 °C). Test conditions of the oscillation amplitude experiments were as follows: frequency from 0.01 to 10 Hz, temperature 20 °C, and strain of 0.1%.

2.5 Stability tests

Stability test was performed at 4, 20 and 40 °C for 3 months in order to investigate the solid state stability after storage. The changes of the texture of emulsions were established by recording flow curves of emulsions after different times of storage at 20 °C.

2.6 Statistical analysis

The effects of biopolymer concentration on rheology and particle size distribution were statistically compared using a one way analysis of variance (ANOVA) followed by the Tukey test. Analysis was performed by SigmaPlot software (version 11.0) and significant differences in results were accepted when $p < 0.05$.

3. Results and discussion

3.1 Morphology of emulsions and size distribution

Figure 1 shows microscopic images of the prepared emulsions. At low OSA starch concentration, the distribution of droplets is characterized by two populations, large and small droplets for different studied oil/water ratios. While the emulsions, with a high concentration of the emulsifying agent, have a small and homogeneous size in most of the formulations.

Figure 2 illustrates the distribution of the mean diameter of emulsions which varies between 1.47 and 9.35 μm ($p < 0.001$). The swollen grains of OSA starch, which give dark particles by the effect of iodine solution, are adsorbed at the oil/water interface and form a protective layer against coalescence around droplets. While the excess of surfactant leads to form a three dimensional network of droplets which prevent their free moving [24,25].

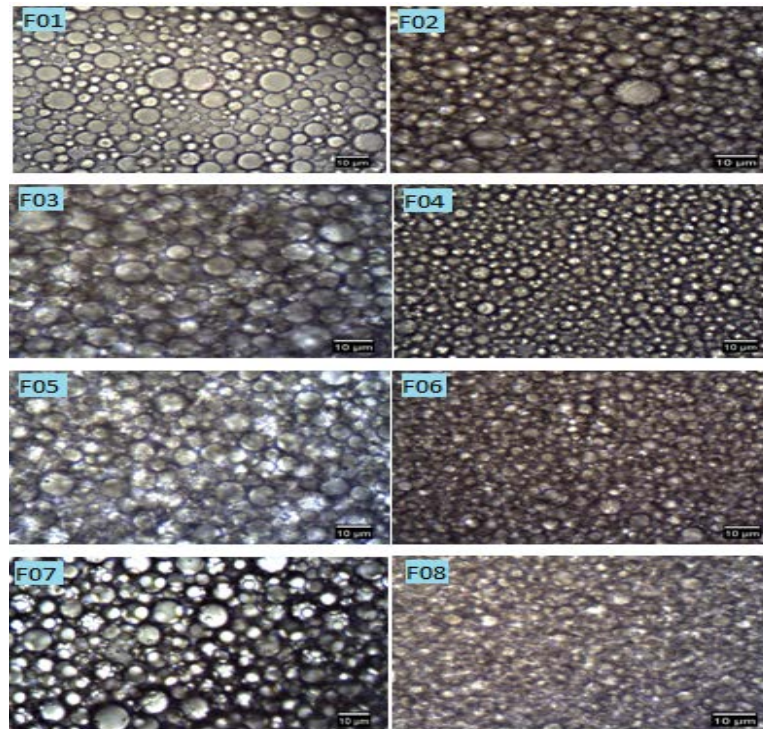


Figure 1. Microscopic images of emulsions 24h after preparation

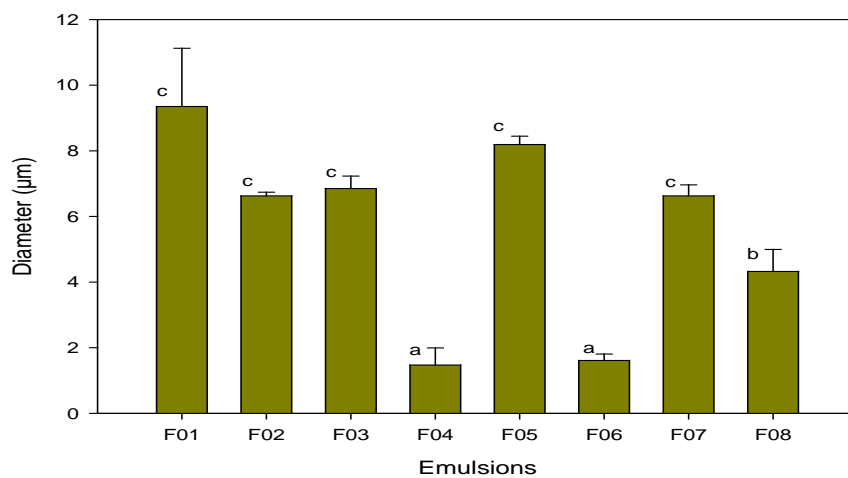


Figure 2. Mean diameter of droplets of different formulations
(Values followed by the same letter are not significantly different ($p > 0.05$))

3.2 Rheological behavior

The variation of the viscosity versus the shear rate (Figure 3) shows two different non-Newtonian behaviors. Hence, formulations with a fraction of oil greater than the fraction of water were consistent and their viscosities were relatively high at rest, but they decreased when the shear rate increases by recording a shear-thinning behavior. In the case of formulations with a fraction of water higher than that of oil, the emulsions had a liquid appearance and their viscosities were low at rest, but they drop rapidly from a critical shear rate value. Consequently, their behavior changed and the variation in viscosity was gradual which meant that the droplets had been destroyed and the viscosity was reduced to the viscosity of the continuous phase [3,26].

When the concentration of OSA starch increased the rheological behavior of the emulsions had been completely changed. They were considered as non-Newtonian fluids with a shear-thinning behavior in which the viscosity decreases as a function of the increase in shear rate. This suggested the formation of a droplet network structure, where the strength of this network depends on OSA starch concentration and the oil fraction. The viscosity of the continuous phase increased when the concentration of the starch reached 10%; it acted as a stabilizer even if the

fraction of the aqueous phase increased. The similar results were found by Song et al. [24] when they used OSA starch as stabilizer of soybean pickering emulsions.

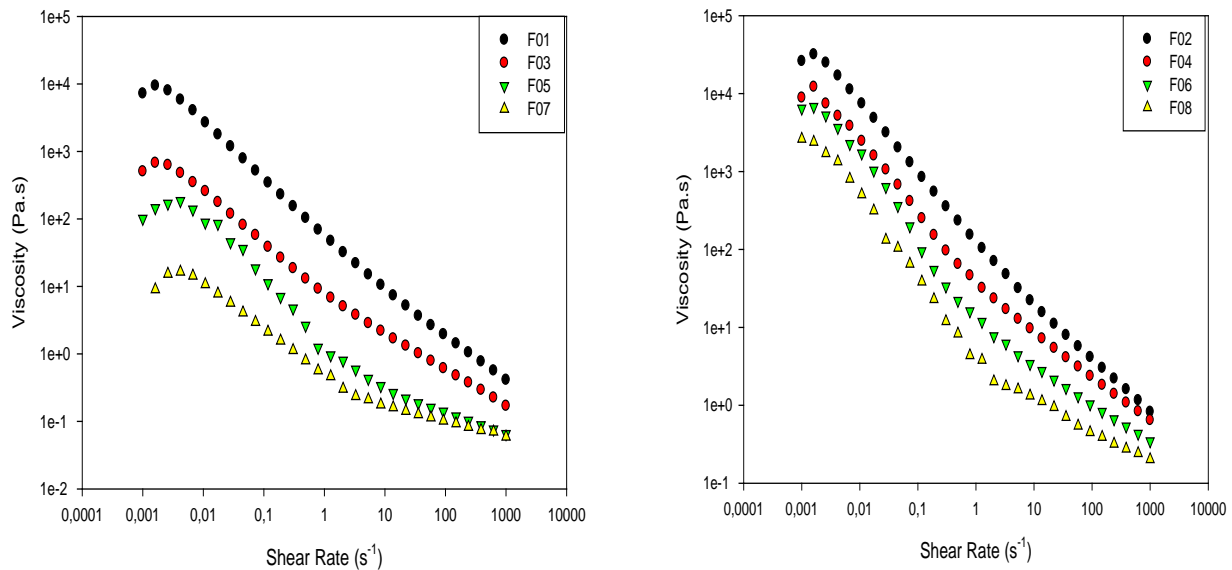


Figure 3. Flow curves of emulsions prepared at different concentrations of OSA starch

In order to compare the rheological characteristics of emulsions, the model of Herschel-Bulkley was used (Eq.1); it describes perfectly the shear-thinning behavior.

$$\tau = \tau_0 + k \cdot \dot{\gamma}^n \quad (1)$$

where τ is the shear stress, τ_0 is the yield stress, k is the consistency coefficient and, n is the flow index.

Table 2 summarizes the results of the evaluation of parameters of Herschel-Bulkley model which were subjected to ANOVA analysis. The yield stress and consistency coefficient showed high values in the case of emulsions prepared with high OSA starch concentrations and, they increased with the increasing of the oil fraction. In the opposite, OSA starch concentration had no effect on the flow index, which decreased with the increasing of the oil fraction.

Table 2. Rheological parameters of Herschel-Bulkley model of emulsions

Formulations	τ_0 (Pa)	k (Pa.s ⁿ)	n	R^2
F01	23.26 ± 1.18^c	32.51 ± 1.33^d	0.35 ± 0.007^a	0.998
F02	72.28 ± 1.76^d	54.00 ± 1.77^e	0.38 ± 0.005^a	0.999
F03	2.02 ± 0.16^a	6.18 ± 0.22^b	0.48 ± 0.007^b	0.999
F04	23.14 ± 0.39^c	16.95 ± 1.001^c	0.52 ± 0.003^c	0.998
F05	1.22 ± 0.07^a	0.29 ± 0.010^a	0.79 ± 0.007^e	0.996
F06	1.22 ± 0.07^b	3.29 ± 0.15^b	0.68 ± 0.006^d	0.992
F07	0.12 ± 0.01^a	0.32 ± 0.01^a	0.74 ± 0.011^e	0.996
F08	5.13 ± 0.05^a	4.79 ± 0.15^b	0.42 ± 0.006^b	0.992

* Values followed by the same letter in the column are not significantly different ($p > 0.05$).

The linear viscoelastic range (LVR) was established by recording the storage modulus (G') and loss modulus (G'') at a fixed frequency (1 Hz). Figure 4 shows that G' remains greater than G'' until the strain exceeds 10% for emulsions prepared with low concentration of OSA starch. However in the case of emulsions prepared with high concentration of OSA, this change occurred when the strain exceeded 1%. After that, the modulus of elasticity dropped and crossed with G'' showing the change in the emulsion behavior which was typical for gel-like emulsions stabilized by a network of droplets; this explains why the values of plateau of G' increased with the increase of the concentration of OSA starch and the oil fraction [18].

Frequency sweep test of emulsions was carried out at a constant strain 0.1% (Figure 5). It was noticed that G' was higher than G'' and independent on the variation of frequency, in the range of 0.1 to 10 Hz, which gave a gel-like behavior in all formulations. Furthermore, G' increased with the increasing of the oil fraction, at low

concentration of stabilizing agent, but at high concentration, the values of G' were comparative and similar. This result confirmed the ability of particles of OSA starch to stabilize emulsions and substitute an important part of oil fraction by the formation of a droplet network [15,24].

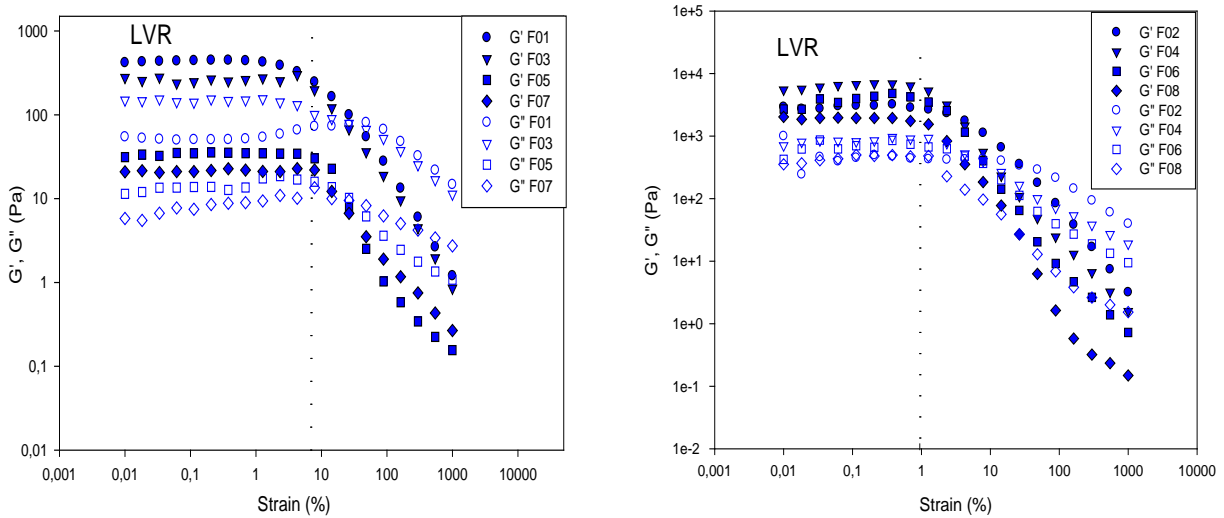


Figure 4. Viscoelastic behaviour of different formulations at constant frequency.

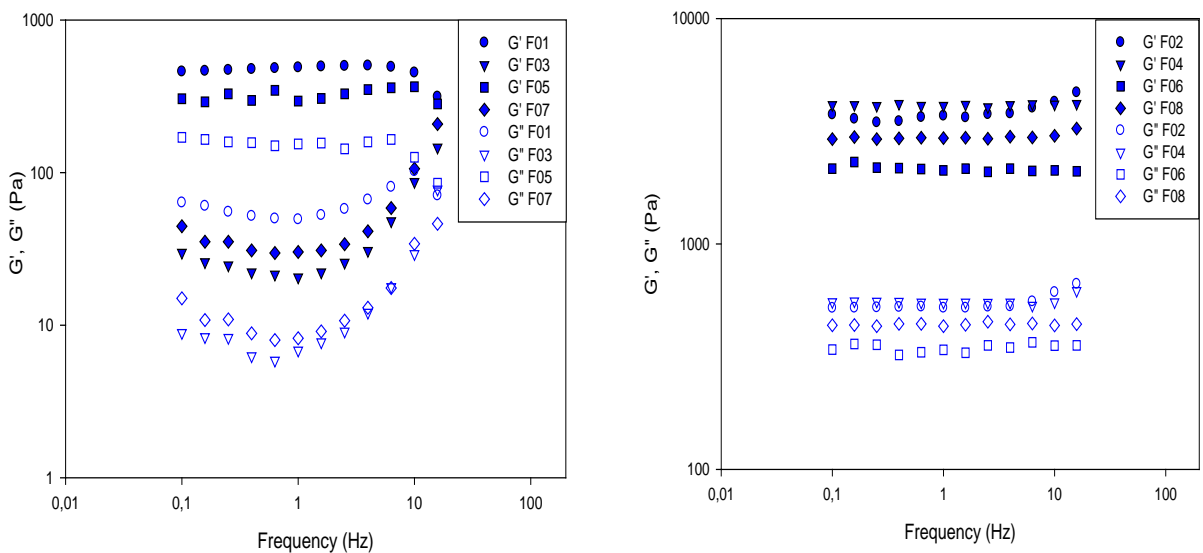


Figure 5. Viscoelastic behaviour of emulsions at constant strain.

3.3 Stability of emulsions

Figure 6 shows the storage stability test results at different temperatures. The formulations containing high concentration of OSA starch exhibited a remarkable stability comparable to those obtained with a concentration of 5% of stabilizing agent.

The formulations F04 and F06 characterized by the medium oily phase content showed the best stability between formulations even at high temperature. At low oily phase content, the formulations had low stability because of the large distance between particles which favours the migration of small to big droplets. When the concentration of OSA starch increased, the macromolecules form a three-dimensional network which made the system stabilized by the steric effect even if the volume fraction decreased [27, 28].

To evaluate the mechanism of instability produced between droplets, flow curves of emulsions were recorded after different storage times. Table 3 summarizes the values of the apparent viscosities of the different emulsions at fixed shear rate (1 s^{-1}). The formulations F01, F02, F04 and F06 showed the best stability ($p < 0.001$) while the apparent viscosities of F03, F05 and F07 increased dramatically after 7 days ($p > 0.05$) which was due to the coalescence. For the formulation F08, the decrease of the apparent viscosity was due to the flocculation of droplets [14,29].

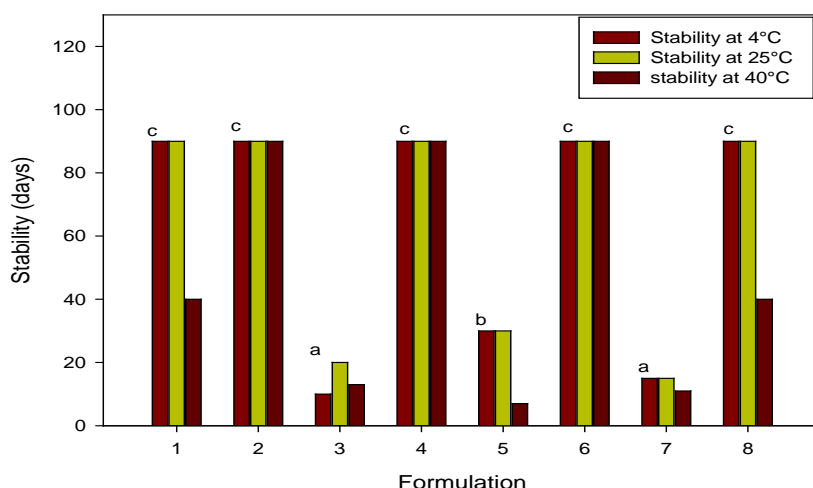


Figure 6. Stability of emulsions at different temperatures
(Values followed by the same letter are not significantly different ($p > 0.05$))

Table 3. Variation of the apparent viscosity of emulsions at different storage times

Storage Time	Apparent viscosities of emulsions at 1 s^{-1}							
	F01	F02	F03	F04	F05	F06	F07	F08
1 day	48.8 ± 2.5^a	108.1 ± 5.8^a	6.9 ± 0.2^a	33.4 ± 2.1^a	0.98 ± 0.04^a	11.8 ± 0.07^a	0.45 ± 0.02^a	18.7 ± 0.9^b
7 days	47.3 ± 2.6^a	69.3 ± 3.6^a	27.8 ± 1.4^b	40.7 ± 2.8^a	10.02 ± 0.6^b	12.4 ± 0.7^a	6.1 ± 0.24^b	2.7 ± 0.06^a
14 days	45.8 ± 2.5^a	82.05 ± 5.1^a	22.7 ± 1.0^b	31.3 ± 0.7^a	5.40 ± 0.1^a	10.8 ± 0.8^a	9.48 ± 0.4^b	0.75 ± 0.3^a

* Values followed by the same letter in the column are not significantly different ($p > 0.05$).

4. Conclusions

The elaborated formulations showed that the more the amount of the oily phase increases the more the viscosity of the emulsions increases which leads to a good stability. As a result, it can be concluded that the oily phase fraction is a major parameter which affects the stability of the formulated emulsions. On the other hand, more stable emulsions were prepared by increasing the concentration of OSA starch even with a high aqueous phase ratio. The most stable emulsions were observed at 60/40 and 50/50 (o/w) fractions with a concentration of 10% of OSA starch. These results were confirmed by the granulometric analysis where a homogeneous distribution of the particles was found, indicating that the obtained systems are mono-dispersed. The rheological study also showed a shear-thinning behavior which could be modelled perfectly by the Herschel-Bulkley model. Dynamic viscoelastic tests confirmed the gel-like behavior of emulsions where it was noticed that G' is higher than G'' and the stability of the emulsions was maintained by the swollen particles of OSA starch which create a three dimensional network with oil droplets.

5. References

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