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Aqueous starch–oil dispersions prepared by steam jet cooking. Starch films at the oil–water interface

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Abstract

Starch–oil composites were prepared by passing aqueous mixtures of starch and soybean oil (100 : 40, by weight) through a steam jet cooker operating under excess steam conditions. Dilution of jet cooked dispersions with a 20-fold excess of water reduced the viscosity and caused a lipophilic fraction with low specific gravity to separate from the dispersion. This fraction could be collected and washed with water without coalescence of oil droplets. Microscopy showed that this fraction was comprised of oil droplets surrounded by thin films of starch at the oil–water interface. The most detailed view of these spherical starch films was obtained by scanning electron microscopy, after isolating films by ethanol precipitation and critical point drying. Films prepared from normal food grade cornstarch, waxy cornstarch and high amylose cornstarch were compared. Interfacial starch films were observed not only when aqueous mixtures of starch and soybean oil were co-jet cooked, but also when starch solutions were first jet cooked and then blended with soybean oil in a separate step. Starch films were also observed with lipophilic materials other than soybean oil, for example, mineral oil, paraffin wax and α-tocopherol. We have considered the question of why these starch films are spontaneously formed at the droplet interface, despite the fact that starch is not surface active and no surface active materials are used during the preparation. A reasonable explanation is provided by the known thermodynamic properties of aqueous polymer solutions at interfaces. Formation of a layer of polymer at an oil–water interface (prewetting) occurs when adsorption of polymer leads to a reduction in interfacial tension and when the solvent for the polymer is relatively poor.

Keywords: Starch–oil composites; Oil–water interface; Steam jet cooking

1. Introduction

Although steam jet cooking has been used for decades to prepare aqueous solutions of starch for industrial applications (Klem and Brogly, 1981), the co-jet cooking of starch with non-starch materials is a relatively new research area that is being investigated at our center as a rapid and continuous method for preparing new starch-based products and derivatives. Previous publications (Fanta and Eskins, 1995;Eskins et al., 1996) describe the preparation, properties and microscopic examination of a new type of starch–lipid composition (Fantesk™) obtained by steam jet cooking starch with a variety of different oils and lipophilic materials. The high temperature and intense mechanical shear during the process of jet cooking dissolves granular starch, reduces its molecular weight (Dintzis and Fanta, 1996; Klavons et al., 1997) and converts the lipid component into droplets having diameters in the 1–10 μm range. Although these compositions typically are made with 20–40 parts lipid per 100 parts of starch, by weight, the lipophilic component does not separate or coalesce, even after prolonged standing; and there is no separation of lipid when jet cooked dispersions are dried. Drum-dried compositions are easily redispersed in water without coalescence of the lipid phase.

The absence of phase separation in these compositions was unexpected. Although the high viscosity of jet cooked starch solutions obviously contributes to the stability of these systems, it was clear that other factors must also be involved. Some possible explanations for the absence of phase separation were suggested in an earlier publication (Fanta and Eskins, 1995). In a later study, transmission electron micrographs showed an apparent boundary layer surrounding the lipophilic droplets that appeared to be an important factor in their resistance to phase separation and coalescence (Eskins et al., 1996). Knutson (1998) recently examined the lipophilic component of jet cooked starch–oil dispersions and also concluded that oil droplets are surrounded by an aqueous starch boundary.

In this publication, we present evidence that lipid droplets

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are indeed surrounded by a thin film of starch at the oil–water interface that forms spontaneously during the preparative process and is not removed by water washing. These interfacial starch films were isolated as discrete entities, their structures were observed using both light and scanning electron microscopy, and their chemical composition was confirmed by FTIR.

2. Materials and methods

2.1. Materials

Normal, unmodified food grade cornstarch and waxy cornstarch (Waxy No. 1) were obtained from A.E. Staley Mfg. Co., Decatur, IL. High amylose cornstarch (Amylomaize VII) was a product of Cerestar (formerly American Maize Products Co.), Hammond, IN. Lipid was extracted from normal, food grade cornstarch with refluxing 95% ethanol for 90 h in a Soxhlet apparatus (Schoch, 1964). The extracted starch was washed with water and allowed to air-dry. Dextran samples (Sigma D-5501, Industrial Grade, MW 5–40 $\times 10^6$ and Sigma D-5376, MW 2×10^6) were obtained from Sigma Chemical Co., St. Louis, MO. Refined food grade soybean oil was Wesson Oil from Hunt-Wesson, Inc., Fullerton, CA. Mineral oil (Sigma M-3516, light white oil, suitable for nujol mulls, no stabilizer added), *n*-hexadecane (minimum 99%) and α-tocopherol (approx. 95%) were obtained from Sigma Chemical Co. Paraffin wax (m.p. 56–61°C) was obtained from Aldrich Chemical Co., Inc., Milwaukee, WI.

2.2. Product preparation

A mixture of 40 g of oil and 1 l of water was stirred at high speed in a Waring blender for about 30 s, and 110 g of cornstarch (moisture content about 10%) was added. The resulting stirred mixture was passed through a Penick & Ford Laboratory Model steam jet cooker operating at 140°C (40 psig steam, back pressure) with a steam line pressure of 70 psig. Pumping rate through the cooker was about 1 l/min. The cooked dispersion (solids content: 9%–10%) was collected in an insulated Dewar flask. Variations in solids content were because of dilution of the cooked dispersion with condensed steam.

Two techniques were used to dilute the jet cooked dispersion for isolation of the lipophilic component. In the ''hot dilution'' technique, 20 g of hot, jet cooked dispersion was diluted to 400 g with hot (100°C) water. The dispersion was gently stirred and was allowed to stand and cool overnight. In the ''cold dilution'' technique, the hot jet cooked dispersion was first allowed to cool overnight; and 10 g of the cooled dispersion was then diluted to 200 g with water at room temperature. The mixture was gently stirred for 2–3 h and was then allowed to stand overnight. Over a period of 12–24 h, a milky, lipophilic layer rose to the surface of each of these diluted dispersions. More rapid separation could be achieved by centrifugation. The lipophilic surface layer was separated from the rest of the dispersion and was washed with water. This lipophilic fraction dispersed rapidly in water with gentle agitation, and was easily separated once again by centrifugation. A precipitated fraction was also obtained after centrifugation of the cold-diluted product prepared from normal food grade cornstarch. The corresponding hot-diluted dispersion did not yield a precipitate.

The hot, jet cooked dispersion remaining after removing material for hot- and cold-dilution was dried on a 45 × 30 cm diameter double-drum drier heated with steam to about 140°C. The resulting flake-like product showed no oil separation and was not oily to the touch. A lipophilic fraction was isolated by mixing 1.5 g of drum dried product with 10 ml of hot (90°C–100°C) water. The resulting paste was diluted with an additional 140 ml of hot water, and the surface layer was separated by centrifugation and washed with water.

When paraffin wax was used, the wax was melted prior to jet cooking by blending with water preheated to 75°C. A portion of the water-washed lipophilic fraction was added to ethanol and critical point dried; whereas another portion was freeze dried. The freeze dried solid was extracted with hexane at room temperature to remove wax, hexane was replaced with ethanol, and the the ethanolic dispersion containing interfacial starch films was critical point dried.

2.3. Light microscopy

Direct visualization of either jet-cooked dispersions or isolated lipophilic surface layers was achieved by placing a small drop of material on a microscope slide and overlaying with a cover glass. Usually the viscosity of the sample supported the cover glass, and no distortion of oil droplets was seen. Otherwise, a bridge cell was formed by placing the sample between two cover glasses positioned 1 cm apart and overlaying a third cover glass to form a chamber. When normal starch was used, the sample was added to a drop of aqueous iodine-KI solution [1% (w/v) I_2 + 1% (w/v) KI] on the slide, which stained the starch blue. Samples of isolated lipohilic surface layers were applied to glass slides, cooled with dry ice, and then lyophilized. A drop of soy oil was then added to form a mounting medium confluent with the oil in the dried sample. Phase contrast microscopy clearly revealed the dried starch films in the soy oil.

2.4. Scanning electron microscopy (SEM)

The best procedure for viewing interfacial starch films isolated from lipophilic surface layers (as judged by the proportion of intact, undistorted, spherical films viewed by SEM) was as follows. Lipophilic surface layers were collected either from diluted dispersions that had been allowed to stand overnight or by centrifugation, as described above. Surface layers were washed three times with water at room temperature to remove soluble starch, diluted with a

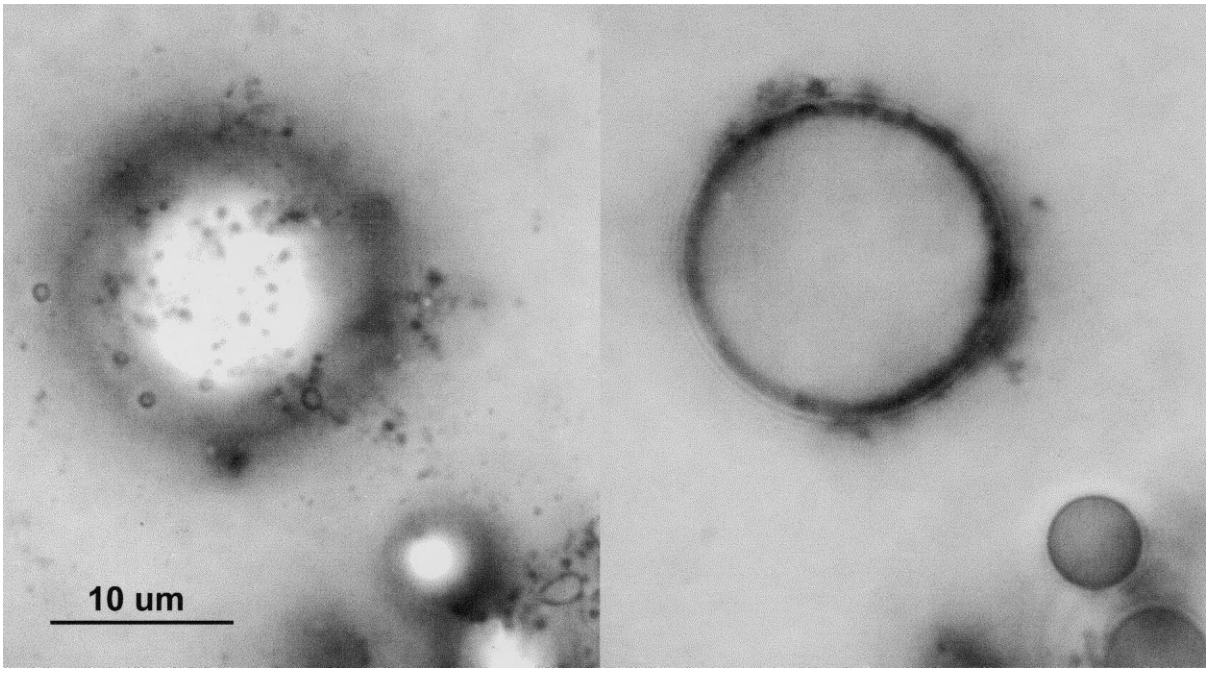

Fig. 1. Light micrograph of washed lipophilic layer obtained from cold dilution of normal cornstarch co-jet cooked with soybean oil. Sample was stained with I_2/KI. Both photographs show the same field but at different focal planes so as to reveal the surface material on the face (left) and at the edge (right) of the central oil droplet.

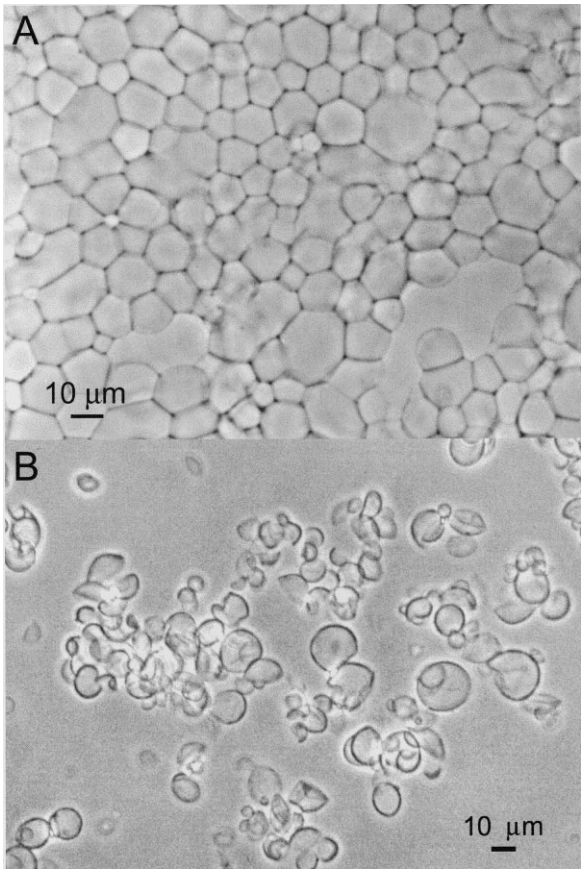

Fig. 2. Light micrographs of washed lipophilic layer obtained from cold dilution of normal cornstarch co-jet cooked with soybean oil. (A) Phase contrast image of freeze dried sample mounted in soybean oil. (B) Phase contrast image of precipitated starch film spheres in ethanol.

small quantity of water for ease of pipetting, and then added to excess absolute ethanol in the proportion of 1 : 200. The included soybean oil readily dissolved into the ethanol, while the interfacial starch film was dehydrated and solidified. The precipitated spherical starch films were allowed to settle for several hours, and the ethanol was then decanted and replaced with fresh absolute ethanol to minimize residual soybean oil and water in the sample. On examination by light microscopy, intact spherical films were observed in the ethanolic dispersion along with broken film fragments. Suspensions of the precipitate in ethanol were applied to aluminum SEM stubs to which conductive tape was attached in a manner designed to contain a small pool of liquid. The stubs were critical point dried in liquid CO_2, sputter-coated with 200 Å gold–palladium, and examined with a JEOL 6400 V scanning electron microscope.

3. Results

Starch–oil composites were prepared by passing aqueous mixtures of starch and soybean oil (100 : 40, by weight) through a steam jet cooker operating under excess steam conditions to achieve maximum shear during cooking (Klem and Brogly, 1981). Although cooked dispersions were smooth and viscous and showed no tendency to phase-separate on standing, 20-fold dilution with water reduced the viscosity and caused a milky, lipophilic layer to separate from the dispersion and slowly rise to the surface over a period of several hours. More rapid separation of this low specific gravity fraction could be achieved

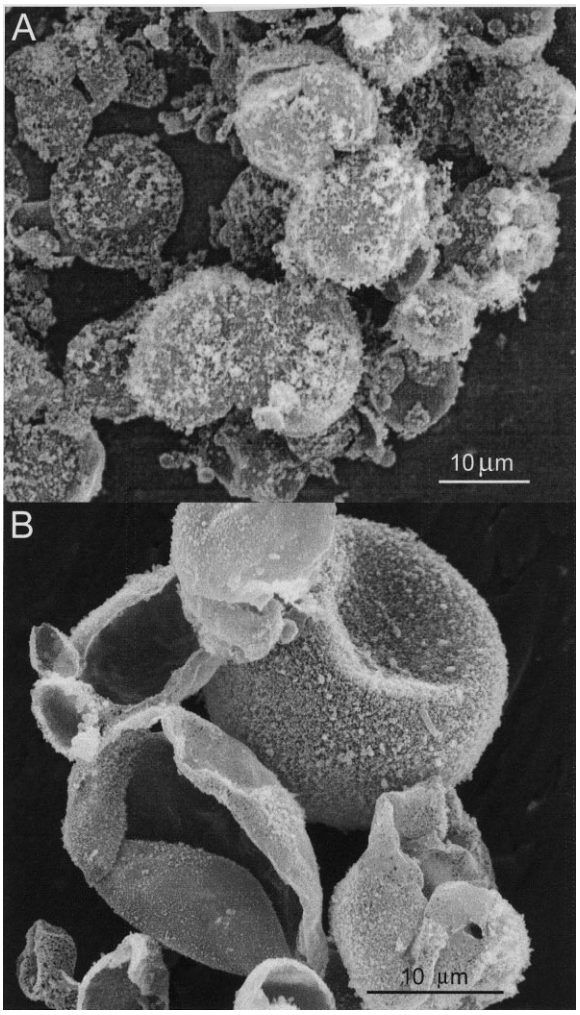

Fig. 3. Scanning electron micrographs of ethanol precipitated fraction of washed lipophilic layer obtained from cold dilution (A) and hot dilution (B) of normal cornstarch co-jet cooked with soybean oil.

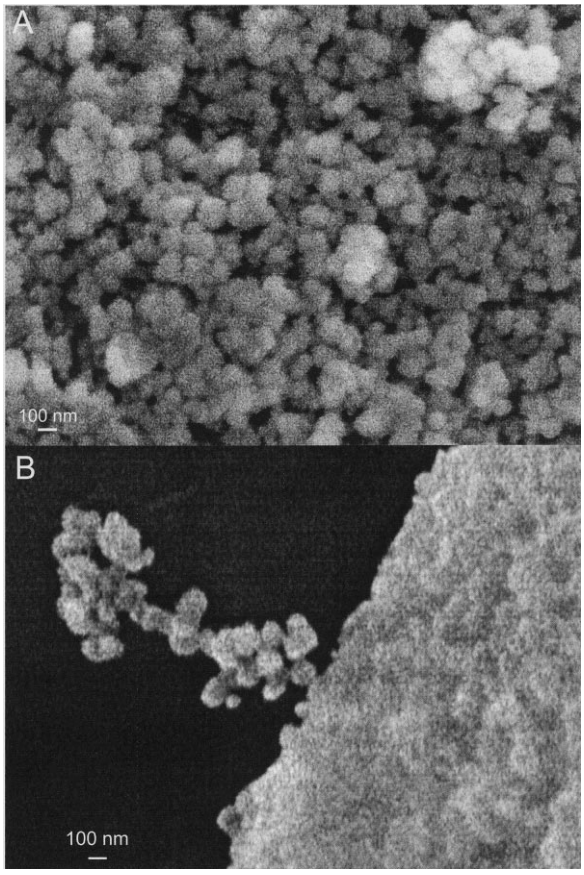

Fig. 4. Same as Fig. 3A, except at higher magnifications. (A) Surface of spherical film showing particles (~ 100 nm) comprising the film surface. (B) Similar particles attached to film surface by amorphous material.

by centrifugation. Typically, 1.4 ml quantities were centrifuged at 4000*g* for 5 min in a microcentrifuge; however, lower *g*-forces could also be used for longer time periods.

Although separation of lipophilic material was not unexpected when viscosities were reduced by dilution with large amounts of water, we were surprised to observe that this milky lipophilic fraction did not coalesce to form a continuous layer of oil when centrifuged, and that this fraction could be redispersed easily in excess water with only gentle agitation. Although examination of the lipophilic phase by light microscopy showed the expected dispersion of oil droplets with diameters in the 10 μm range, the droplets appeared to be coated with a thin film of starch at the oil–water interface. These interfacial films could be stained blue with iodine/KI solution (see Fig. 1). Consistent with formation of a starch film, we observed that the droplets did not coalesce on the microscope slide, even after prolonged standing. Further evidence for starch-coated droplets was obtained by freeze-drying the lipophilic phase on a glass microscope slide. The phase contrast image of the residue mounted in soybean oil (Fig. 2A) revealed discrete films or shells with diameters about the same as the oil droplets shown in Fig. 1. These films have a hexagonal appearance because of their close packing. An FTIR spectrum of the residue obtained by freeze drying showed strong soybean oil absorption and only weak absorption because of starch. Extraction of the freeze-dried residue with hexane and ethanol removed nearly all of the soybean oil and yielded a solid product, the FTIR spectrum of which showed strong starch absorption and only weak carbonyl absorption due to residual soybean oil. Light micrographs (photographed in ethanol) of the spherical starch films that precipitated when the washed lipophilic fraction was added to ethanol are shown in Fig. 2B.

The most detailed views of starch films were obtained by SEM of ethanol-washed and critical point dried products. Interfacial starch films appeared as mixtures of intact spherical shells, partial spheres and sphere fragments. Some hollow spherical particles had a reticulated or lacey surface structure. Fracture and fragmentation of starch films and reticulation of the film surface probably occurs during dehydration of the starch film with ethanol followed by critical

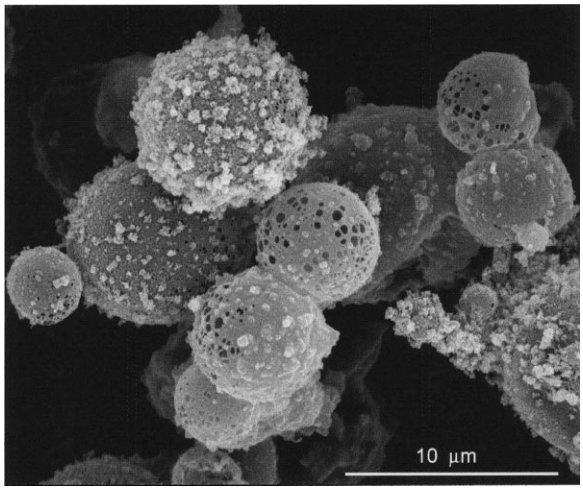

Fig. 5. Spherical films precipitated in ethanol from lipophilic layer collected from a sample prepared by reconstituting drum-dried starch–oil composite in hot water.

point drying. The shape and texture of interfacial starch films is often best revealed by these partial spheres and fragments, and the contrast seen between the rough outer surface and relatively smooth inner surface of these spherical films is consistent with the accretion of starch onto the smooth surfaces of lipid droplets.

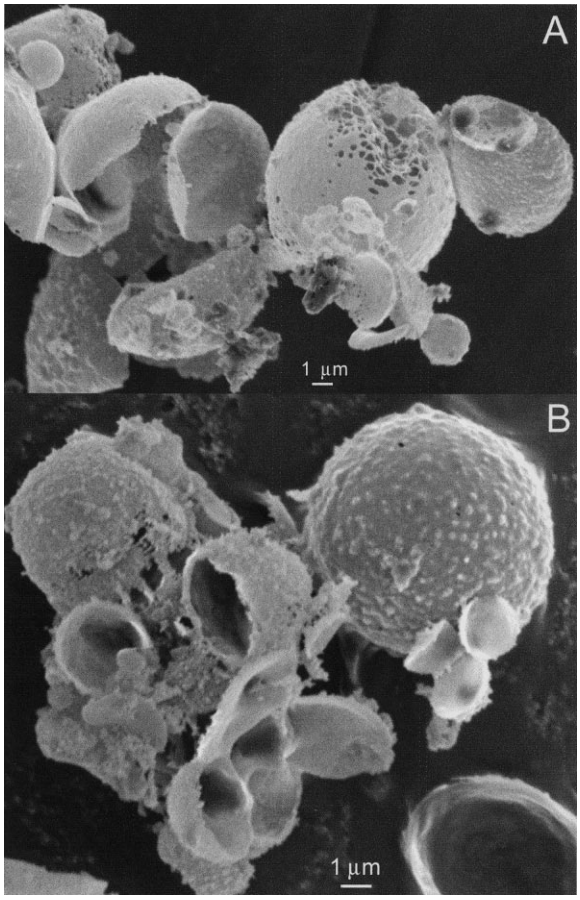

Fig. 6. Same as Fig. 3, except using waxy cornstarch. (A) Cold dilution. (B) Hot dilution.

Jet cooking soybean oil with normal food grade cornstarch, having an amylose content of about 25% produced the starch films shown in Fig. 3A (cold dilution) and Fig. 3B (hot dilution). These dilution techniques are described under Materials and Methods. Film surfaces were smoother when the hot dilution technique was used. At high magnification (Fig. 4A), SEM showed a fine structure consisting of spherical particles having diameters in the 100 nm range. This is roughly the same order of magnitude as the radius of gyration reported by Klavons et al., (1997) for amylopectin. Particles of this type were also seen on film surfaces as bead-like projections (Fig. 4B). When the jet cooked dispersion was drum-dried, and drum-dried material was then reconstituted by stirring with hot water, the starch films shown in Fig. 5 were obtained. Interfacial starch films are thus sufficiently stable to survive the process of drum drying followed by redispersion of the dried product in water. It is interesting that these spherical starch films exhibit a wide variation in surface texture.

Analogous films obtained from cold- and hot-diluted dispersions prepared from waxy cornstarch, which contains little or no amylose, are shown in Figs. 6A,B. These films appear to be smoother and thinner than those obtained from normal cornstarch, perhaps because aqueous solutions of amylopectin form gels at a slower rate than amylose and do not retrograde. Starch films obtained from a preparation made with high amylose cornstarch (amylose content, about 70%) are shown in Fig. 7A and were isolated by hot-dilution. These films have rougher textures than those obtained from normal food grade cornstarch, probably caused by retrogradation and rapid gelling of amylose. The cold-dilution technique could not be used with high amylose starch, because the jet cooked dispersion formed a rigid gel when cooled that could not be redispersed in excess water unless high-shear mixing was used. Interfacial films were also obtained when high molecular weight dextran (MW 5–40 $\times$ 10^6) was used in these preparations in place of starch (Fig. 7B).

Interfacial starch films were observed not only when aqueous mixtures of starch and soybean oil were were co-jet cooked, but also when starch solutions were first jet cooked and then blended with soybean oil in a second step. Fig. 8A shows starch films obtained by cold dilution of a dispersion prepared in this manner from normal food grade cornstarch. High-shear mixing was carried out in a Waring blender at about 90°C to avoid retrogradation of amylose. Experiments with waxy cornstarch showed that interfacial starch films are also formed when jet cooked starch solutions are cooled to room temperature prior to blending with soybean oil (Fig. 8B).

Formation of interfacial starch films takes place not only with soybean oil but also with other lipophilic materials. The interfacial films formed are shown for: mineral oil (Fig. 9A); *n*-hexadecane (Fig. 9B); *alpha;*-tocopherol (Fig.

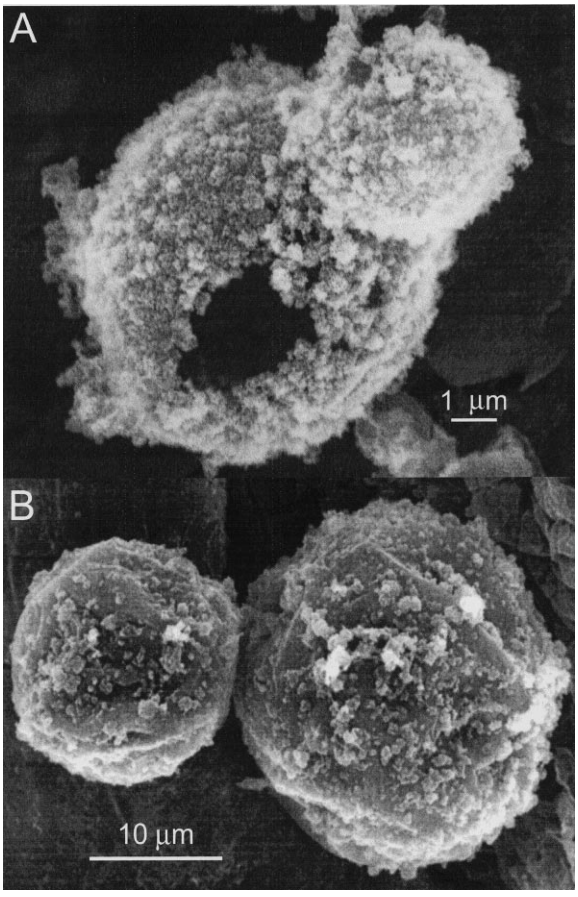

Fig. 7. Same as Fig. 3, except sample obtained by co-jet cooking soybean oil with (A) high amylose starch and (B) high molecular weight dextran, MW $5–40 \times 10^6$.

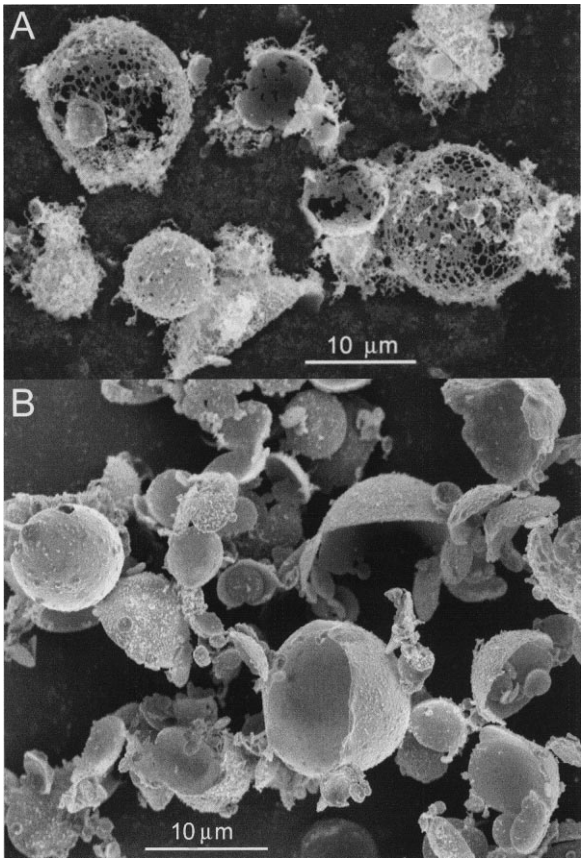

Fig. 8. Same as Fig. 3, except soybean oil was blended into (A) a hot dispersion of normal cornstarch immediately after jet cooking and (B) a dispersion of waxy cornstarch after cooling to room temperature.

9C) and paraffin wax (Fig. 10). Extraction of normal food grade cornstarch with ethanol to remove the small amount of lipid material normally associated with these starches had no effect upon film formation at the mineral oil–water interface (SEM not shown). Since paraffin wax is a solid at room temperature, we were able to isolate spherical particles of starch-coated wax by simply freeze drying the cold-diluted lipophilic fraction after washing with water. These particles (Fig. 10A) were smoother and showed less surface structure than the same particles isolated by addition to excess ethanol followed by critical point drying (Fig. 10B). Although ethanol does not dissolve paraffin wax, we are uncertain whether paraffin wax is being removed from these particles by supercritical CO_2 during the critical point drying process. When the freeze-dried product was extracted with hexane, paraffin wax was dissolved, leaving behind the interfacial starch films shown in Fig. 10C.

Although this study has only dealt with characterization of the low-specific gravity, lipophilic components of these aqueous starch–oil dispersions, another fraction comprised of spherical particles about 5–10 μm in diameter was also obtained as a precipitate (Fig. 11A), when cold-diluted preparations made from normal food grade cornstarch were centrifuged. Although these particles have some similarity in size and shape to the spherical interfacial starch films shown earlier, their properties are quite different. First of all, these particles have specific gravities greater than one, since they precipitate from an aqueous dispersion. Second, most particles appear to be solid throughout and exhibit strong birefringence when dried. SEM revealed no fractured spheres or starch film fragments, even after a deliberate attempt was made to fracture this material by high-shear homogenization. Finally, a precipitate was observed only when the product was prepared from an amylose-containing starch, and when the cold-dilution technique was used. Since a precipitate somewhat similar in appearance was formed from normal food grade cornstarch that was jet cooked in the absence of oil (Fig. 11B), this precipitated fraction no doubt contains retrograded amylose. Formation of spherocrystallite particles by high-temperature retrogradation of maize starch solutions has been reported by Davies et al., (1980). It is also possible that some of these particles result from the formation of thick starch coatings around small oil droplets to yield starch–oil composites with a high enough specific gravity to make them precipitate from water. Additional work is needed to characterize this fraction.

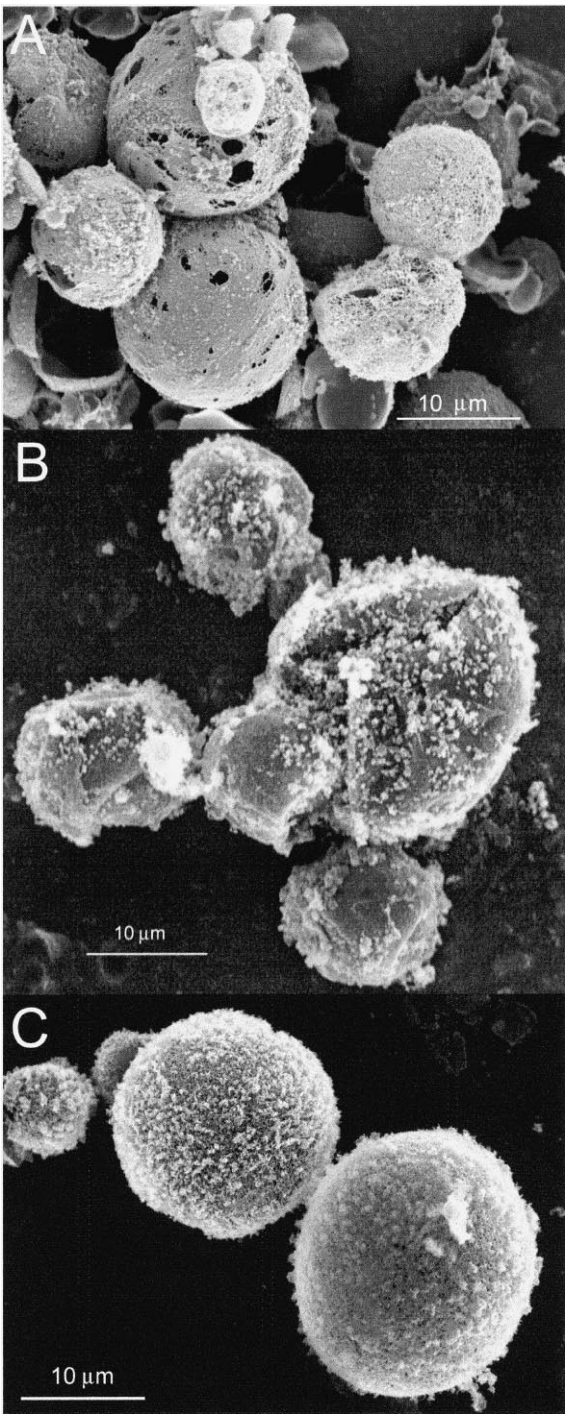

Fig. 9. Same as Fig. 3A, except mineral oil (A), *n*-hexadecane (B), or α-tocopherol (C) were used as the lipophilic component instead of soybean oil.

4. Discussion

Definitive evidence that the particles observed by microscopy are indeed films of starch from the oil–water interface, and not simply fragments of gelled or retrograded starch, is the fact that these particles were isolated from water-washed lipophilic layers having specific gravities less than that of water. Repeated washing with excess water would have removed any loosely-bound starch fragments or gel from this low-density layer. It was surprising that starch films were not easily separated from the droplet interface and were not removed when dispersions were diluted with water, and the lipophilic layer was water-washed. These films were formed not only by jet cooking aqueous mixtures of starch and oil, but also when starch solutions were prepared by jet cooking in a separate step and then blended with oil under high-shear conditions. Formation of interfacial starch films was not limited to soybean oil, but also occurred with a variety of different hydrophobic materials, such as paraffin oil. The thickness and appearance of starch films seen under SEM varied with the amylose content of the starch and also with the dilution technique used to isolate the lipophilic fraction (i.e., hot-dilution versus cold-dilution). Although no attempt was made to quantify film thickness, it appeared that starch films were thinnest and had the smoothest surfaces when waxy starch was used, and when the lipophilic fraction was isolated by hot-dilution. Films obtained from high amylose starch exhibited a rough surface texture. Under high magnification, SEM revealed that these starch coatings were comprised of spherical particles with radii in the 100 nm range.

The formation of polymer films at oil–water interfaces is well known and has been observed with proteins and with certain hydrocolloid gums that possess a high level of surface activity (Kitchner and Mussellwhite, 1968; Dickinson et al., 1988; Fisher and Mitchell, 1992). Gum Arabic (or gum acacia) is an example of a surface active hydrocolloid that is widely used in food products; and there is evidence that its surface activity results from chemically bound protein (Dickinson, 1988). Photographs of gum Arabic film at an oil–water interface have been published (Shotton and White, 1963). Emulsan is another example of a surface active polysaccharide, and this material derives its surface activity from fatty acid esters linked to the polysaccharide chain (Zosim et al., 1982).

Although most polysaccharides have little or no surface activity, they are frequently used to stabilize oil–water emulsions, especially in foods (Sharma, 1981). Some basic principles and mechanisms related to their use as stabilizers have been reviewed (Dickinson, 1988; Dickinson, 1995). Water-soluble polysaccharides can inhibit the coalescence of oil droplets and thus function as emulsion stabilizers by increasing the viscosity of the continuous water phase. An increase in viscosity can also facilitate the conversion of large drops of oil into small droplets by high-shear mixing when the emulsion is prepared (Gaonkar, 1991). Polysaccharides can also stabilize emulsions, in the presence of surface-active materials such as proteins, by adsorbing onto the primary layer of surfactant at the oil–water interface to yield a secondary layer of adsorbed polymer (Bergenstahl, 1988;Dickinson, 1994). Addition of

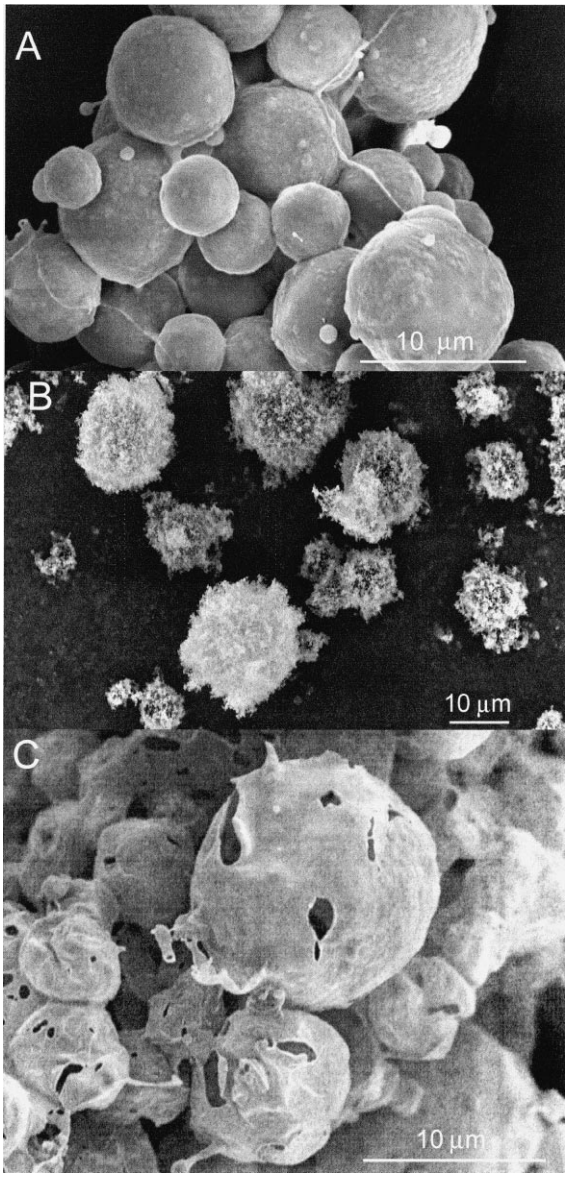

Fig. 10. Lipophilic fraction obtained from normal cornstarch co-jet cooked with paraffin wax (cold dilution). (A) Lipophilic fraction isolated by freeze drying. (B) Lipophilic fraction isolated by adding to ethanol and critical point drying. (C) Freeze-dried lipophilic fraction extracted with hexane/ethanol and then critical point dried.

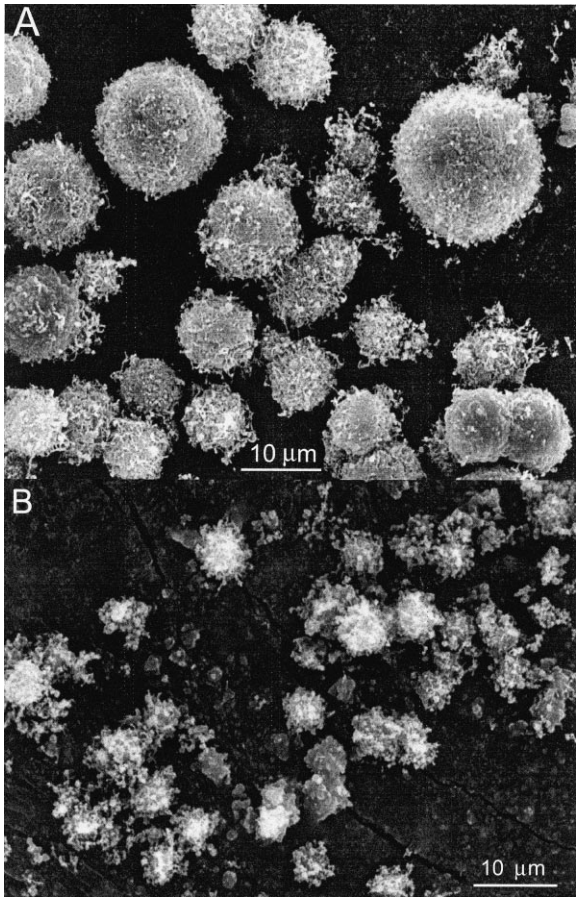

Fig. 11. (A) Precipitated solid obtained when the cold-diluted normal cornstarch/soybean oil dispersion was centrifuged. The precipitate was washed with water, diluted with excess ethanol and critical point dried. (B) Precipitated solid obtained in the same manner from a jet cooked dispersion of normal cornstarch prepared in the absence of soybean oil.

water-soluble polysaccharide to an oil–water–protein mixture can stabilize emulsions by causing a protein-rich phase to separate from water solution, owing to thermodynamic incompatability between the two biopolymer solutions (Tolstoguzov, 1993; Dickinson and McClements, 1995). This separated phase can then coat the oil droplets with a thick layer of protein on top of the surface active protein layer already present at the oil–water interface.

In addition to stabilizing emulsions, polysaccharides can also reduce the stability of emulsions by causing oil droplets to flocculate, by either a bridging or a depletion flocculation mechanism (Dickinson, 1988; Dickinson and Stainsby, 1988). For example, Dickinson and Galazka (1992) showed that hexadecane emulsions were destabilized when either dextran or amylopectin was used in conjunction with bovine serum albumin.

Although formation of starch films at the droplet–water interface accounts for the unusual stability of our jet cooked dispersions, we must consider the question of why these films spontaneously form during the preparative process, despite the fact that starch is not surface active and no surface active materials are used in our preparations. Since interfacial films are formed from waxy starch as well as from amylose-containing starch varieties, retrogradation and rapid gelling of the amylose fraction cannot be a major factor responsible for film formation. Also, the formation of interfacial starch films around droplets of paraffinic materials, such as mineral oil, *n*-hexadecane and paraffin wax, rules out the theory that surface active monoglyceride impurities in commercial soybean oil (Gaonkar, 1989) are responsible for film formation. Effects caused by the small quantities of surface-active lipid normally present in commercial cornstarch are also unlikely; since removal of

this lipid fraction by ethanol extraction had little effect upon film formation.

Although more research is needed, the known thermodynamic properties of aqueous polymer solutions at interfaces (Glasstone, 1947; Koberstein, 1987) seems to provide the best explanation for the formation of these interfacial starch films. Interfacial tension is a measure of the excess free energy arising from the formation of an interface between oil and water. The formation of an oil–water interface when a coarse mixture of oil and water is reduced to an aqueous dispersion of oil droplets thus requires that work be performed on the system. If a solute, such as a water-soluble polymer, is present in such a two-phase system, this solute can preferentially adsorb at the interface separating the two phases, provided that the adsorption of solute results in a reduction in interfacial tension. The amount of solute adsorbed at the interface is directly related to the magnitude of this reduction in interfacial tension. These principles have been discussed in relation to the use of food hydrocolloids and proteins as emulsion stabilizers (Dickinson, 1988; Dickinson et al., 1988). Specifically, these polymers in solution become increasingly associated or aggregated as the solvent quality, as measured by the Flory–Huggins parameter (P), becomes poorer. In a good solvent for the polymer, P is approximately zero; and its value increases as solvent quality becomes poorer. When P exceeds a certain critical value (which reaches its lowest value of 0.5 at infinite polymer chain length) the system separates into two phases: one rich in solvent and the other rich in polymer. In a system containing dispersed particles, such as oil droplets, this polymer-rich phase will accumulate at the interface separating oil and the aqueous polymer solution to form a relatively thick interfacial layer of polymer. This phenomenon is known as *prewetting*, and is favored when the interaction between polymer and the oil–water interface is energetically favored over the interaction between polymer and water. Prewetting can thus take place when the solvent is relatively poor (with a P value only slightly less than the critical value) or when P is greater than the critical value and the amount of hydrocolloid in solution is lower than the solubility limit. To quote Dickinson (1988) : ''The effect of the interface in prewetting is to perturb the local thermodynamic state of the system into the two-phase region by acting as a template for polymer precipitation, when the bulk composition is in the one-phase region but is close to the phase coexistence curve. The polymer concentration in the prewetting layer is generally high; so, if the polymer forms a gel phase at high concentrations, the surface will be covered by a thick gel-like film whose thickness depends on bulk polymer volume fraction.''

Dickinson (1988) also states that ''the hydrocolloid polymer will not in general be accumulating at a bare particle surface, but at one already covered with more surface-active material, i.e., the proteinaceous emulsifier. That is, the role of the hydrocolloid in this instance is to form a secondary stabilizing layer around the dispersed particle or droplet.'' If this statement is true, how do we account for the formation of these interfacial starch films in the absence of any material having surface-active properties? There is probably a combination of factors responsible for the prewetting behavior of starch. First of all, the molecular weight of amylopectin is extremely high. After steam jet cooking under conditions similar to those used in this study, Klavons et al., (1997) observed M_w values for waxy cornstarch that ranged from 33 to 93 $\times$ 10^6, depending upon the type of measurement used. Despite its high molecular weight, amylopectin is completely dissolved in water under the high temperature and high-shear conditions of the jet cooking process. Water, however, is a relatively poor solvent for starch, compared, for example, to DMSO (Callaghan and Lelievre, 1985; Moates et al., 1997); and amylopectin molecules in water solution are known to form large hydrogen-bonded aggregates (Callaghan and Lelievre, 1985). Aggregate formation probably begins shortly after the starch solution exits the jet cooker, and possibly as soon as the temperature of the starch solution drops from 140° to 100°C. These aggregates have only limited water solubility, because of their large molecular size, and therefore will have a strong tendency to separate from solution and thus accumulate at the oil–water interface. The thermodynamic incompatability of amylose and amylopectin in water solution (Doublier and Llamas, 1993) would also favor the separation of amylopectin aggregates. The submicron spherical particles that comprise these interfacial starch films (Fig. 4A) could thus be aggregates of amylopectin molecules. These aggregates can also contain hydrogen-bonded amylose, when amylose is present in the starch sample used. The ability of both amylose and amylopection to form strong hydrogen bonds and gel networks is probably responsible for the reluctance of these films to dissolve or separate from the interface during isolation and water washing of lipophilic fractions.

The importance of molecular weight in the formation of stable interfacial polysaccharide films is suggested by experiments carried out using dextran as the polysaccharide instead of starch. Although film formation was observed with a high molecular weight industrial grade of dextran with molecular weight 5–40 $\times$ 10^6 (Fig. 7B), a dextran sample with lower molecular weight (MW 2 $\times$ 10^6) produced no observable film at the oil–water interface.

5. Conclusions

When a two-phase mixture of starch, water and oil is passed through a steam jet cooker at high temperature and steam pressure, the viscous, cooked dispersion is stable and does not phase-separate, even after prolonged standing or drying. When the viscosity is reduced by dilution with excess water, a low-density, lipophilic fraction separates from the dispersion; and this layer can be collected and freed of loosely-bound starch by water washing. Although

this fraction is lipophilic, it disperses easily in water with only gentle agitation. Light microscopy and SEM indicate that this lipophilic fraction is comprised of oil droplets coated with thin films of starch at the oil–water interface. These films are firmly bound to the oil droplets and are not removed from the interface during isolation and water washing. The spontaneous formation of interfacial starch films during the preparative process explains the unusual stability of jet cooked starch–oil dispersions and the fact that coalescence of oil droplets is not observed.

We have considered the question of why starch films are spontaneously formed at the droplet interface, despite the fact that starch is not surface active and no surface-active materials are used during the preparation. A reasonable explanation is provided by the known thermodynamic properties of aqueous polymer solutions at interfaces. Formation of a relatively thick layer of polymer at an oil–water interface (i.e., prewetting) occurs when the interaction between dissolved polymer and the interface is energetically favored. Prewetting is thus observed when adsorption of polymer leads to a reduction in interfacial tension and when the solvent for the polymer is relatively poor. Prewetting can take place more readily with starch than with other water-soluble hydrocolloids because water is a relatively poor solvent for the starch macromolecule. Also, amylopectin has a very high molecular weight, is completely dissolved by the jet cooking process, and has a strong tendency to form hydrogen-bonded aggregates having limited water solubility. The tendency of starch to form gel networks accounts for the fact that interfacial starch films are not removed during isolation and water washing of lipophilic fractions.

We are currently examining a number of end-use applications for these starch-coated lipophilic droplets in the areas of cosmetics, foods, drug delivery and adhesives.

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