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Surfactant-free formulations employing a synergistic complex between a hydrophobically modified, cationic cellulose ether and amylose

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Synopsis

This paper describes the preliminary development of a non-traditional emulsifier system, with characteristics similar to a standard oil-in-water emulsion system, employing a unique polysaccharide/polysaccharide complex formed by non-covalent crosslinking of a hydrophobically modified, water-soluble cationic cellulose ether (Quatrisoft® Polymer LM-200, polyquaternium-24) with amylose, a component of normal potato starch. Six oil-in-water emulsions were prepared with different emollients or pigments, and their stability was monitored by lack of separation over a period of six weeks at room temperature. A prototype skin lotion was also prepared, and monitored for stability over a six-week time period at both room temperature and 45°C via a Brookfield viscometer.

INTRODUCTION

The most common, commercially useful emulsions are typically oil-in-water (1,2). The oily discontinuous phase in personal care applications is typically some type of emollient or conditioner, of which many are well known (3). For typical, unadulterated water, stable suspensions are generally impossible for any extended period of time. An emulsion formed from oil and water will usually coalesce quickly back to two layers unless the droplets of oil are very small, as occurs, for example, in microemulsions (4). Even in the case of microemulsions, the desire for the oil and water to separate will typically cause separation over time.

In order for water to be useful as a continuous phase, its gross molecular structure must be altered so as to improve its ability to suspend the oily phase. Classically, the water structure is altered by addition of molecules that possess both hydrophilic (water-loving) and hydrophobic (water-avoiding) components, i.e., surfactants (5). Surfactants used in personal care products can also have profound physiological effects on the proteins and lipids that comprise human skin and hair (6–9). The body generally responds quickly to

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such assaults by replacing the lost oils and proteins (10). However, sometimes the body is not able to respond as expected and the normal healthy appearance of the skin becomes red and irritated (11–13).

One response to this deficiency has been to employ polymeric thickners that help to stabilize emulsions by imparting a yield point to the aqueous continuous phase. Two excellent examples of such polymers are the naturally occurring, marine-derived polysaccharide, xanthan, and the synthetically derived, hydrophobically modified poly(acrylates) (14,15). Both of these polymers can suspend oil droplets indefinitely when used at low concentration with or without additional surfactants. Both of these polymeric species, and in fact, most polymers that function in this capacity, are typically anionic polymers. They generally require the addition of base to promote their thickening and suspending characteristics. Because they are anionic in use, these polymers have little desire to interact with the proteins of the skin and hair.

Cationic polymers, on the other hand, are very well known for their unique conditioning benefits because these polymers do have a natural attraction for the skin and hair (16–18). However, there are very few cationic polymers that can also be used to impart a yield point to the aqueous continuous phase of an emulsion. Some cationic polymers are capable of thickening aqueous mixtures, but they are not necessarily efficient rheology modifiers and they are rarely used as conditioning polymers (19,20). On the other hand, some unique, hydrophobically modified cationic conditioning polymers, while showing some thickening abilities, do not impart a yield point to aqueous solutions. In particular, polyquaternium-24 has demonstrable hair and skin conditioning benefits but does not impart a yield point to aqueous solutions (21).

Recently, we reported a unique, synergistic polysaccharide/polysaccharide blend wherein polyquarternium-24, when carefully blended with amylose, a linear, naturally occurring polysaccharide available from normal potato starch, affords an unusually thickened, aqueous, three-dimensional polymer network complex (22). This network creates a yield point in aqueous solutions when the polyquaternium-24 and amylose are used at low concentrations in very specific weight ratios. We wish to expand on the properties of this unique polymer blend by demonstrating that by employing the polyquaternium-24/amylose complex, stable surfactant-free formulations can be developed. The aqueous complex can suspend a variety of oils and finely ground solid materials such as titanium dioxide. The combined use of the cationic conditioning polymer to also stabilize surfactant-free emulsions shows that this hydrophobically modified cationic polymer is quite versatile.

EXPERIMENTAL

MATERIALS

The preparation of the complex formed between polyquaternium-24 and amylose is described elsewhere (22). In summary, a hot aqueous solution of polyquaternium-24 is carefully blended with a hot aqueous solution of potato amylose, such that the resultant mixture is composed of 1.0 part polyquaternium-24, 0.25 part amylose, and 98.75 parts deionized water. The hot mixture is then carefully cooled, which allows the polymer complex to form, building aqueous viscosity. Additional raw materials used in the study are summarized in Table I. The emulsion samples were made using a Talboy overhead stirrer at 15 rpm, and the viscosity of the samples was measured using a standard Brookfield DV-II+ viscometer, using spindle # 3 at 25°C. The oven samples were placed in a Blue M® Stabil-Therm oven, and the photos of formulations were taken via a Polaroid camera attached to an Olympus AH-2 model microscope.

RESULTS AND DISCUSSION

FORMATION OF OIL SUSPENSIONS

An initial study was done to examine the ability of the aqueous polyquaternium-24 and amylose blend to suspend water-insoluble oils and solids by using various conditioning and emollient oils as well as titanium dioxide at 1, 5, and 10 wt % concentrations. The oils and solids were directly dispersed without strict control of biological conditions into 1% aqueous mixtures of the complex at 25°C (the complex itself must be created at higher temperatures) (22). The samples were then left undisturbed for six weeks at room temperature. The samples were visually inspected weekly for signs of incompatibility. The results of this initial study appear in Table II.

Several of the emulsified samples remained clearly suspended at room temperature for six weeks. In particular, the emulsified silicon oils showed good resistance to oil and water partitioning. Microscopic examination after two weeks of one such 10% emulsion containing cyclomethicone is shown in Figure 1. The appearance of the various-sized oily droplets is evident in the photo. Samples of emulsions prepared using polyquaternium-24 without the carefully blended amylose separate in a matter of days. The combination of the hydrophobic, cationic cellulose ether and amylose is clearly needed to maintain stable suspensions. It appears that the polyquaternium-24/amylose complex can suspend oils at room temperature at oil concentration levels at least as high as 10% without separation between the oil and water phases even after a six-week time period.

We also examined the suspension of micronized TiO_2 in the complex. Figure 2 shows the fine dispersion of micronized TiO_2 in the complex. This suspension also contained

Table I
Experimental Raw Materials

INCI name	Trade name	Company
Dimethicone	Amersil®	OSi
Cyclomethicone	Amersil VS®	OSi
Hydroxylated milk glycerides	Cremerol HMG®	Amerchol
Polyquaternium-24	Quatrisoft® Polymer LM-200	Amerchol
Isononyl isononanoate	Salacos® 99	Nisshin
Caprylic capric triglyceride	Myritol® 318	Henkel
Hydrogenated polyisobutene	Panalene®	Amoco Chemical
Methyl gluceth-10	Glucam® E-10	Amerchol
Diazolidinyl urea	Germaben® II-E	Sutton Laboratories
DMDM hydantoin	Glydant®	Lonza
Glycerin	Glycerin	Mallinckrodt
Titanium dioxide	Titanium dioxide	Aldrich
Amylose	Amylose	Sigma Chemical

Table II
Results of a Six-Week, Room-Temperature, Emulsion-Stability Study of Various Oils and Solids Suspended in the Aqueous Polyquaternium-24/Amylose Complex

Emulsified component	Weight percent	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6
Mineral oil	1	•	•	•	•	•	•
	5	•	•	•	•	•	SU
	10	•	•	•	•	•	•
Isononyl isononanoate	1	•	•	SU	SU	SU	SU
	5	•	•	•	SU	SU	SU
	10	•	•	•	•	•	•
Dimethicone	1	•	•	•	•	•	SU
	5	•	•	•	•	•	•
	10	•	•	•	•	•	•
Cyclomethicone	1	•	•	•	•	•	•
	5	•	•	•	•	•	•
	10	•	•	•	•	•	•
Caprylic capric triglycerides	1	•	•	SU	U	U	U
	5	•	•	SU	U	U	U
	10	•	•	SU	U	U	U
Hydrogenated polybutene	1	•	•	•	•	•	•
	5	•	•	•	•	•	SU
	10	•	•	•	•	•	•
Titanium dioxide	1	•	•	•	SU	SU	U
	5	•	•	•	•	•	•
	10	•	•	•	•	•	•

Slightly unstable (SU): Material is starting to separate.
Unstable (U): Material has separated into two distinct phases.
(•) indicates a stable emulsion.

approximately 1% dimethicone, the droplets appearing as dark circles against the white TiO_2 particles. What is particularly intriguing is the apparent ability of the complex to prevent the TiO_2 and the oil from agglomerating. The TiO_2 remains well dispersed in the mixture.

PREPARATION OF SKIN LOTION FORMULATIONS USING THE POLYQUATERNIUM-24/ AMYLOSE COMPLEX

Following the completion of the initial oil-suspending study, a prototype skin lotion formulation was developed using the polymer complex (Table III). The simple prototype formulation was developed by taking advantage of the functional attributes of various well-known skin conditioners. Hydroxylated milk glycerides and glycerin are excellent emollients and humectants, respectively. Dimethicone oil is the primary skin conditioner, but the polyquaternium-24 also has demonstrable feel properties. Methyl gluceth-10 was added to impart rheological control to the slightly pituitous polyquaternium-24/amylose complex.

These formulations impart a soft, lubricious feel to the skin with little tackiness during drying. Once dried, the formulations leave a soft afterfeel. The formulations showed no signs of pilling upon application, an occurrence sometimes noted in anionic poly(acrylate) thickeners. We investigated different application methods, including pump sprays

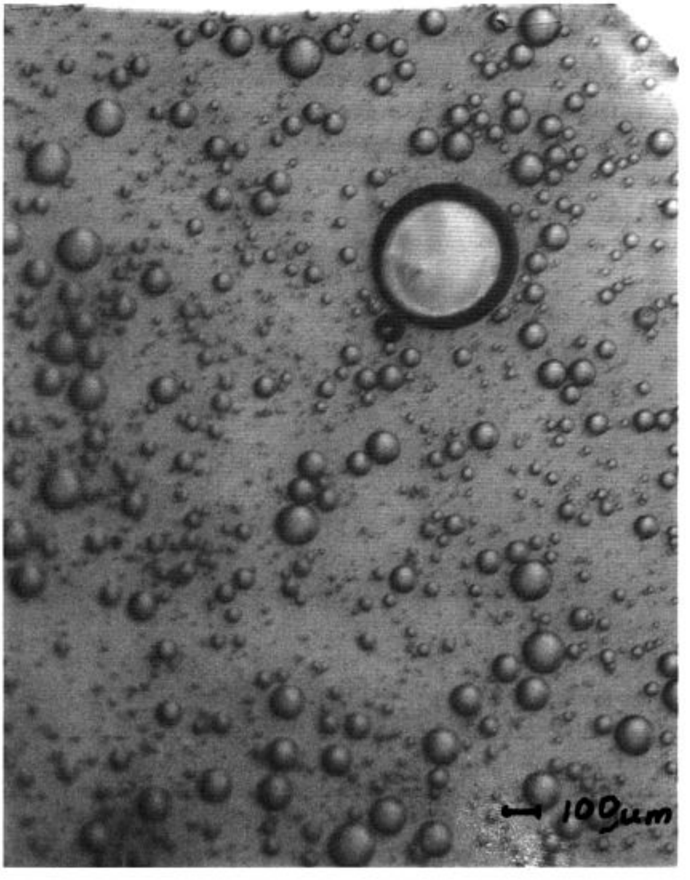

Figure 1. Photomicrograph of 10% suspension of cyclomethicone in a 1% aqueous solution of the polyquaternium-24/amylose complex (magnified 37.5×).

and pouring devices, and found that the shear-thinning complex allows for the lotions to be easily pumped or poured.

PRESERVATIVE AND COMPATIBILITY STUDY OF SURFACTANT-FREE FORMULATIONS

Polysaccharides, especially starch, are particularly susceptible to contamination, and dissolved starch is an excellent bacterial growth medium. Breakdown of the amylose component of the polyquaternium-24/amylose complex results in eventual collapse of the stabilizing matrix. To examine the coalescence stability of the formulation described in Table III, four similar samples were prepared. Two were stored at room temperature, and two were stored in a 45°C oven for six weeks to mimic accelerated aging. Diazolidinyl urea and DMDM hydantoin were examined as potential preservatives. The samples were visually inspected for signs of creaming or separation, and the viscosity was monitored weekly. The results of both the oven-accelerated and room temperature studies are summarized in Figures 3 and 4.

After one week, all four samples showed a slight initial decrease in viscosity, which was

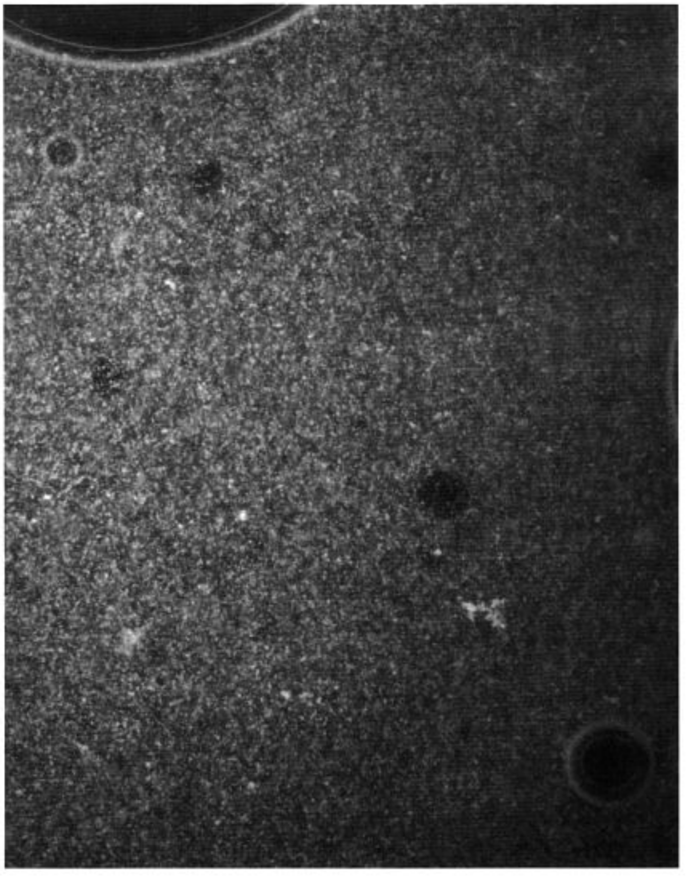

Figure 2. Photomicrograph of a 1% suspension of dimethicone and 0.5% titanium dioxide in a 1% aqueous solution of the polyquaternium-24/amylose complex (magnified 75×).

Table III
Prototype Skin Lotion Formulation Employing Polyquaternium-24/Amylose Complex[a]

Dimethicone	(Amerchol)	5.00%
PQ-24/amylose complex[b]		91.50%
Hydroxylated milk glycerides	(Amerchol)	2.00%
Glycerin	(Mallinckrodt)	0.50%
Methyl gluceth-10	(Amerchol)	0.50%
Titanium dioxide	(Aldrich)	0.50%
Preservative[c]		q.s.

[a] *Procedure:* Disperse micronized titanium dioxide into previously prepared PQ-24/amylose complex at room temperature, followed by dispersion of the dimethicone oil into the complex. Add molten hydroxylated milk glycerides (previously melted in a 45°C oven prior to use). Stir 15 minutes, add glycerin and methyl gluceth-10, and stir for an additional 15 minutes. Add preservative and stir for one hour.
[b] Complex comprises approximately 0.9% Quatrisoft and 0.2% amylose.
[c] DMDM hydantoin at 0.40% or diazolidinyl urea at 1%.

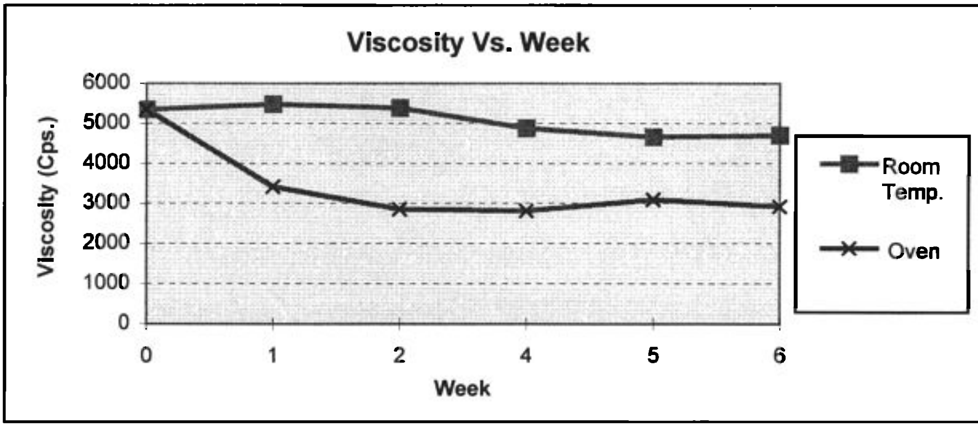

Figure 3. Stability of individual formulations preserved with DMDM hydantoin at room temperature and 45°C.

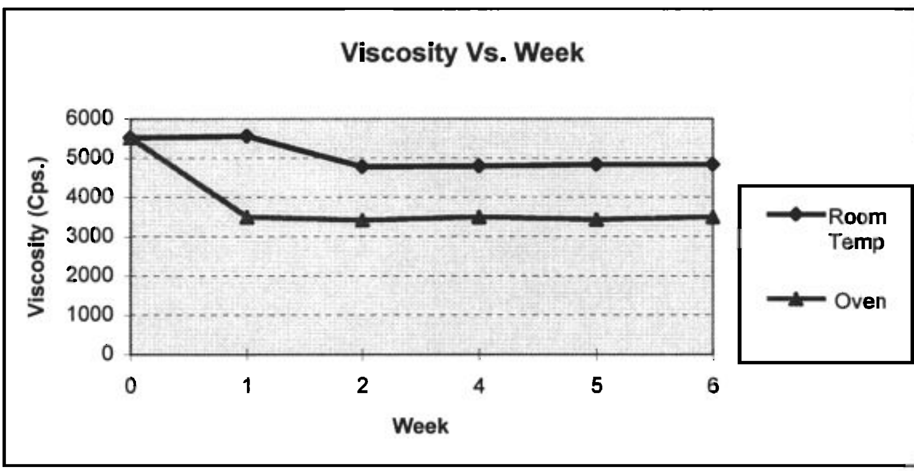

Figure 4. Stability of individual formulations preserved with diazolidinyl urea at room temperature and 45°C.

more pronounced in the oven-accelerated samples. However, none of the samples showed any indications of creaming, and in fact, after this initial drop, the viscosity stabilized. We attribute the initial viscosity drop to a possible rearrangement of the polyquaternium-24/amylose complex brought on by the temperature of the oven. Once the formulations stabilized to their environmental temperatures, they remained stable for the extent of the test.

CONCLUSIONS

Although the use of traditional emulsifiers brings many attributes to the science of cosmetic chemistry, one cannot overlook potential detrimental effects and possible irritancy upon application. In this paper, the idea of surfactant-free formulations has been presented using a unique complex formed by non-covalent crosslinking of a hydrophobically modified, water-soluble cationic cellulose ether, polyquaternium-24, with amylose. Oils can be successfully suspended, and remain suspended for up to a six-week time period both at room and elevated temperatures. The complex also has the ability of suspending other agents such as titanium dioxide in combination with the oils. By taking advantage of the stablizing ability of this complex, one can potentially mitigate the detrimental effects brought on by amphiphilic emulsifiers and still develop successful skin care formulations.

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