

OPTIMIZING PERFORMANCE WHEN USING POLYMERS IN SURFACTANT-BASED CLEANSING PRODUCTS

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Introduction

Acrylate polymers are widely used in surfactant cleansing systems for rheology modification, suspension and stabilization. These polymers can enhance sensory properties, such as product appearance, texture, pourability and flow, ease of spreading and distribution and skin feel – properties critical to success in the marketplace. Further, they offer advantages vs. salt thickening and other rheology modifiers in improved flow (smooth vs. stringy or sticky) and appearance, suspension and stabilization.

Staying ahead in today's marketplace requires focus on creating the best formulations and on efficient production, especially for high volume, high throughput products like shampoos, body washes and liquid soaps. Critical decision points include total surfactant actives concentration and the type of surfactants to be used; desired pH; desired viscosity and flow characteristics; the need for suspension of insoluble particles; whether the finished product is to be clear or opaque; anticipated processing conditions and storage and handling capabilities.

The objective of this work is to assist formulators and process engineers in the scale-up and manufacturing of surfactant-based cleansing products which employ polymeric rheology modifiers. Polymer properties, thickening mechanisms, formulating conditions and processing parameters most critical to optimizing performance and throughput are presented for:

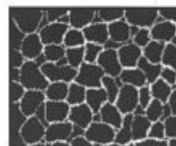
- Traditional, highly crosslinked polyacrylic acid (PAA) polymers
- Hydrophobically-modified, crosslinked acrylate copolymers such as Acrylates/C10-30 Alkyl Acrylate Crosspolymer
- Liquid rheology modifiers such as Acrylates Copolymer
- Liquid, hydrophobically-modified, amine functional and crosslinked Polyacrylate-1 Crosspolymer

General Polymer Properties

General polymer properties in formulations are presented in Table 1, showing physical form, flow profile, relative viscosity, relative yield value, clarity, relative ion tolerance and relative shear tolerance.

Thickening and stabilization mechanism in surfactant systems

Traditional crosslinked PAA polymers build viscosity through charge-induced polyelectrolyte chain expansion and hydrogen bonding. This creates a network of swollen, microgels tightly packed in close contact ("space-filling mechanism"). It is well known through the literature¹ that driving forces in polymer-surfactant interactions include hydrophobic modification and electrostatic interaction. In cleansing formulations, microgel interactions are influenced by the presence of surfactant micelles which also occupy space in the solution. Anionic surfactant micelles repel anionic polymer microgels, thus reducing contact and viscosity. A high relative viscosity and yield value profile can deliver adequate thickening and stabilization. These polymers can form hydrogen bonds with formulation ingredients such as EO and/or PO nonionic surfactants, fatty acids and polyols. Thickening occurs over time through the formation of large, cooperative structures, but rarely affects the final formulation.



With Acrylates/C10-30 Alkyl Acrylate Crosspolymer, thickening occurs upon neutralization due to charge repulsion (hydrodynamic volume expansion). Again, it is primarily the physical packing of polymer microgels which provides viscosity and suspending capabilities. This polymer has moderately high ion tolerance and thus, maintains good integrity in the presence of electrolytes.

Though not associative by chemistry, Acrylates Copolymer shows unique behavior. It interacts with surfactant systems in a way that is pH dependent. Thickening occurs via hydrodynamic volume expansion and through interaction with surfactant micelles. The resulting three-dimensional network enables viscosity to be maintained in the presence of higher electrolyte content. The polymer builds viscosity at pH >6, but in the presence of typical anionic and amphoteric surfactants, a patented "back-acid thickening" mechanism enables viscosity and suspension to be increased through the addition of an acid, like citric acid. The polymer offers synergistic thickening with surfactants and salt.

Polyacrylate-1 Crosspolymer presents a novel thickening mechanism for lower pH formulations or in formulations containing cationic ingredients. This cationic-compatible polymer builds viscosity through the mechanisms of hydrodynamic volume expansion, plus *controlled* hydrophobic association which occurs when pH is reduced to <6. The thickening, suspension and stabilization properties of this polymer can be further optimized in neutralized surfactant-based cleansing systems through the addition of a base, such as sodium hydroxide, using a process known as “back-alkaline thickening”. This polymer also offers synergistic thickening with surfactants and salt when formulated with suitable surfactant systems.

Formulating Conditions & Processing Parameters

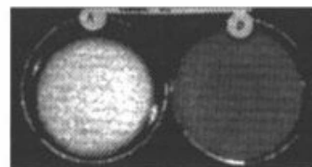
Dispersion

One way of improving the manufacturing throughput of cleansing products is to reduce cycle time. This is possible by reducing polymer dispersion time or making pre-dispersions. Traditional carbomer powders typically require careful addition to the water portion of the formulation, have a longer hydration time and require vigorous agitation. Acrylates/C10-30 Alkyl Acrylate Crosspolymer is a rapid self-wetting polymer that requires no dispersion agitation. In a lab comparison at 25°C, the wetting time using 0.5 wt.% polymer for traditional carbomer was >50 minutes, while Acrylates/C10-30 Alkyl Acrylate Crosspolymer wet in just 3 minutes. Wetting time can be further reduced by increasing water temperature, with best results between 25 - 50°C. Further, this polymer can be dispersed at concentrations up to 6.0 wt.% and still remain pumpable. Liquid rheology modifiers, such as Acrylates Copolymer and Polyacrylate-1 Crosspolymer, are even simpler. Specifics on dispersion method and dispersion times are presented in Table 2.

Order of Addition

Particularly with liquid rheology modifiers, such as Acrylates Copolymer, order of addition is critical in getting both the best performance and the greatest efficiency. Order of addition and other efficiency tips are shown in Table 3.

Yield value is the initial resistance to flow under applied stress. Yield value – not viscosity – is the dominant factor in determining suspending ability. This is critical in product formulation. Model cleansing formulations will be shown. Yield value, and the advantages of using Acrylates Copolymer are clearly demonstrated in the Pearlized 2-in-1 Conditioning Shampoo (SH-0024 A&B), where the three-dimensional network enables the mica to maintain a stable, brilliant appearance over time.



Storage, Handling and Cleaning Procedures

When using liquid polymers, it is extremely important to use clean storage vessels and transfer equipment, and to maintain temperature exposure within recommended limits. Care should be taken to avoid forming foam during material transfer, to avoid conditions exposing the polymer to high shear and to avoid use of piping susceptible to temperature extremes. With rheology modifier polymers, thorough cleaning should be done after manufacturing, assuring tanks and transfer lines are well cleaned. The use of good manufacturing practices will assure trouble-free performance, minimize batch-to-batch variation, reduce unnecessary strain on equipment and avoid rework. Recommended storage and brief handling procedures are presented in Table 4, and cleaning procedures are referenced in Table 5.

An often overlooked issue that can impact polymer performance in cleansing applications is when technology is transferred from an operation experienced in handling and formulating with newer polymer technologies (such as Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Acrylates Copolymer or Polyacrylate-1 Crosspolymer) to one which is less experienced. To achieve optimal results, these novel polymers require correct handling, designed specifically for their molecular architecture. Understanding this can assure optimized performance when using polymers in surfactant-based cleansing product formulations.

¹ E. D. Goddard and K P. Ananthapadmanabhan, Ed., *Interactions of Surfactants with Polymers and Proteins*, Ch. 5, (1993).

² US patents 6767878 and 6897253.

³ Patent-pending.

Table 1: General Polymer Properties in Surfactant-Based Cleansing Formulations

Polymer Type (INCI Designation)	Physical Form	Flow Profile	Relative Viscosity	Relative Yield Value	Clarity	Relative Ion Tolerance	Relative Shear Tolerance
Carbomer	Traditional Powder	Short	High	High	Moderate	Low	Low
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	Powder with Self-Wetting Technology	Medium to Long	Medium to High	High	Very High	Moderately High	Low
Acrylates Copolymer	Liquid Dispersion, 30% solids in water	Long	Low to Medium	High	Very High	High	High
Polyacrylate-1 Crosspolymer	Liquid Dispersion, 20% solids in water	Medium	Low to Medium	Medium	High	Moderately High	High

Table 2: Formulating Conditions & Processing Parameters: Dispersion Method and Time

Polymer Type (INCI Designation)	Recommended Dispersion Method	Recommended Dispersion Temperature	Typical Dispersion Time (0.5% at 25°C) (Lab scale)
Carbomer	Sift slowly into water with vigorous agitation (800-1200 rpm). Eductor recommended. Water flow must commence before addition of polymer to eductor funnel.	Cold to Ambient Water Temperature	~20 minutes (with eductor and vigorous agitation) ~50 minutes (without eductor or agitation – not recommended)
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	Sprinkle onto surface of water and allow to hydrate. Self-wets in 3-5 minutes. After hydration, begin gentle agitation.	25 - 50°C Heat will increase dispersion rate.	~3 minutes
Acrylates Copolymer	Add polymer to (deionized) water of the formulation.	Ambient to 30°C. If necessary to add to hot system, dilute before adding.	Instant (liquid dispersion polymer)
Polyacrylate-1 Crosspolymer	Add polymer to (deionized) water of the formulation.	Ambient to 30°C	Instant (liquid dispersion polymer)

Table 3: Order of Addition and Efficiency Tips

Polymer Type (INCI Designation)	Typical Use Level (Wt. % Actives) in Cleansing Formulations	Order of Addition	Efficiency Tips
Carbomer	1.0%	Sift slowly into water with vigorous agitation (800-1200 rpm) using eductor. Once hydrated, add oil phase. Neutralize. Then add surfactants and ancillary ingredients.	Eductor and vigorous agitation
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.8 – 1.0%	Sprinkle polymer on surface of (deionized) water of formulation. After fully wet, begin gentle agitation. Keep agitation to a minimum to avoid air entrapment, while adding remaining ingredients. Neutralize (pre or post neutralization possible, depending on needs of formulation).	Best efficiency in systems using low to moderate level of surfactant actives (<12 wt.%) and at pH 5.0.

Table 3: Order of Addition and Efficiency Tips (continued)

Acrylates Copolymer	1.0 – 3.0% for clear products; 1.5 – 1.8% for pearlized products	Add polymer to (deionized) water of the formulation. Add primary surfactants. Neutralize to a pH of 6.5. Add remaining (specialty) surfactants. Add conditioning and ancillary ingredients, and if desired, appearance modifiers. Add fragrance, dyes and preservatives. Adjust final pH with citric acid solution ("back-acid" process). Add sodium chloride to adjust viscosity (if necessary). <i>Order of addition is very important.</i>	Efficiency can be improved by including betaines in combination with typical sulfates and sulfonates. Best efficiency in systems using moderate to high level of surfactant actives (15-23 wt.%). "Back-acid thickening" and/or sodium chloride can be used to increase efficiency.
Polyacrylate-1 Crosspolymer	1.0 – 1.5%	Add polymer to (deionized) water of the formulation. Add primary and secondary surfactants. Add conditioning and ancillary ingredients, fragrance, dyes and preservatives. Neutralize to pH <6.0	Efficiency can be improved by including betaines in combination with typical sulfates and sulfonates. Best efficiency in systems using moderate to high surfactant actives (15-23 wt.%). "Back-alkaline thickening" and/or sodium chloride can be used to increase efficiency.

Table 4: Storage & Handling Procedures

Polymer Type (INCI Designation)	Storage	Shelf Life (Under Recommended Storage Conditions)	Comments
Carbomer	Store in clean, dry environment. Containers should be kept tightly closed to avoid moisture pickup. Avoid dusting.	2 years	Polymer is supplied at <2% moisture content; above 2% may cause clumping or difficulty in dispersion.
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	Store in clean, dry environment. Containers should be kept tightly closed to avoid moisture pickup.	2 years	Polymer is supplied at <2% moisture content; above 2% may cause clumping or difficulty in dispersion.
Acrylates Copolymer	Store in unopened containers at 5-30°C. Do not FREEZE. Recommended to use in full drum quantities.	9 months. Optimal storage temperature is 21°C.	Best results if product is filtered before use. Conditions exposing the polymer (as supplied) to high shear should be avoided. Keep storage vessels and transfer equipment clean. Prompt flushing of transfer equipment is recommended.
Polyacrylate-1 Crosspolymer	Store in unopened containers at 20-30°C. Product is freeze-thaw stable as supplied. Recommended to use in full drum quantities.	6 months.	Mix (do not filter) prior to use. To avoid skimming and product discoloration, do not open drums until ready to use. Polymer contains amine groups which can discolor when exposed to the atmosphere; this does not impact polymer performance.

Table 5: Cleaning Procedures

Polymer Type (INCI Designation)	Recommended Procedure (Overview)
Carbomer	Oil-free formulas should be cleaned with hot saline solution. Emulsion formulas should be cleaned with hot detergent solution. Use warm to hot alkaline water (65°C). Raise pH using caustic. Add ionic detergent such as sodium tripolyphosphate. Agitate for 30 minutes. Turn agitation off & drain. Scrap loose deposits. Repeat 2-3 times.
Acrylates/C10-30 Alkyl Acrylate Crosspolymer	Oil-free formulas should be cleaned with hot saline solution. Emulsion formulas should be cleaned with hot detergent solution. Use warm to hot alkaline water (65°C). Raise pH using caustic. Add ionic detergent such as sodium tripolyphosphate. Agitate for 30 minutes. Turn agitation off & drain. Scrap loose deposits. Repeat 2-3 times.
Acrylates Copolymer	Storage tanks should be cleaned by thorough flushing or using the caustic fill and soak method. If buildup occurs on smaller pieces of equipment, it can be removed by soaking in 1.5% caustic solution. The caustic solution can be heated to 75°C. Cleaning of transfer piping and pumps can be minimized by leaving lines full (with no air pockets). If not kept full, transfer lines should be flushed well after each use.
Polyacrylate-1 Crosspolymer	Storage tanks should be cleaned by thorough flushing or using an acidic solution to soak and then flush. If buildup occurs on smaller pieces of equipment, it can be removed by soaking. Transfer lines and equipment should be flushed well after each use.