More than rheology: multi-functional polymers with superior aesthetics in hair care applications

Julie Shlepr, Global Director of Marketing, Personal Care, and

*Julie Castner, Research Manager I, Noveon, Inc.**

Keywords

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Introduction

Aesthetic properties are some of the most important features of personal care products. While any shampoo can cleanse the hair, those that look attractive at the point of sale, and are more pleasant to use, are the ones that ultimately win market share. Thus, the need to enhance the sensory experience, beyond focusing solely on product functionality, is a critical challenge facing formulators. This is why, for example, surfactants are not used solely for cleansing, but also to deliver richer, more billowy lather and to minimize the risk of irritation.

Similarly, rheology control agents are not used solely for thickening. Today's rheology modifiers must offer not only the functional aspects of thickening, suspension and stabilization, but must also provide enhanced appearance to the finished product; superior flow and pour properties; a smooth, light, cushiony feel in use and a pleasant after-feel.

This article presents three novel technologies designed to exceed expectations for functionality as well as sensory attributes: Acrylates Copolymer, for use in surfactant-cleansing systems, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, for use in surfactant-cleansing or aqueous-based systems, and Polyacrylate-14, for use primarily in aqueous-based systems (1).

Acrylates Copolymer

Carbopol® Aqua SF-1 Polymer (INCI: acrylates copolymer) is an alkali-swellable, lightly crosslinked acrylic emulsion polymer designed for use in high surfactant content (12-30 wt%) cleansing applications. The polymer is supplied as a liquid, and offers instant dispersion in water and low viscosity properties (before neutralization) for easy handling and low energy consumption.

Typical properties are shown in Table 1:

Table 1.

Appearance	Milky white liquid
Viscosity (mPa·s)	10
Active polymer (% by weight)	30
pH	3.0

Although not an associative polymer by chemistry, it does show some associative behavior and favors surfactant structuring. Thickening occurs via hydrodynamic volume expansion and through interaction of the hydrophobic portion of the polymer backbone with surfactant micelles. This three-dimensional structuring network builds viscosity and other rheological properties.

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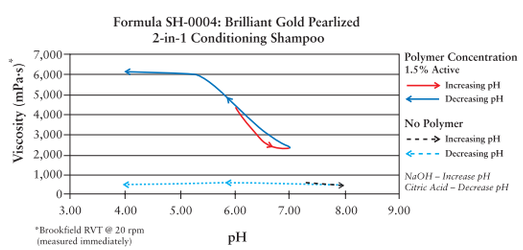
In most situations, the polymer can be added to the available water in a formulation with gentle mixing at the start of the batching process. At this point, the pH will be around 3, resulting in low viscosity. Upon addition of base, the polymer will be neutralized, resulting in immediate increase in suspending properties and viscosity.

In the presence of typical anionic and amphoteric surfactants, Noveon's Acrylates Copolymer displays another feature, the ability to 'back acid thicken' while maintaining the inherent properties of the polymer. After the polymer-surfactant formulation has been neutralized (by adding base to reach pH 6.5), the pH can then be lowered through the addition of an acid, such as citric acid, to give a resulting increase in suspension and viscosity (Figure 1). Other acids give similar behavior.

Figure 1.



INCI Name / Trade Name	Weight %
PART A	
1. Deionized Water	15.80 (q.s.)
2. Acrylates Copolymer (30%), *Carbopol®* Aqua SF-1 Polymer*	5.00
3. Ammonium Lauryl Sulfate (30%), *Sulfochem™* ALS Surfactant*	40.00
4. Ammonium Laureth Sulfate (3 mole, 28%), *Sulfochem™* EA-3 Surfactant*	20.00
5. Sodium Hydroxide (18%)	0.80 (q.s to pH 6.5)
PART B	
6. Ammonium Xylene Sulfonate (40%), *Stepanate® AXS*	2.50
7. PEG-7 Glyceryl Soyate, *Chemonic™* SI-7 Surfactant*	4.00
8. Disodium Cocoamphoacetate (50%), *Monateric CLV*	4.00
9. Amodimethicone (and) Trideceth-12 (and) Cetrimonium Chloride, *Dow Corning® 2-1894 Microemulsion*	3.00
PART C	
10. Deionized Water	2.00
11. Mica (and) Titanium Dioxide (and) Iron Oxides,** *Cloisonne® Sparkle Gold Mica*	0.20
PART D	
12. Diazolidinyl Urea, Propylene Glycol, Methylparaben, Propylparaben, *Germaben® II*	1.00
13. Fragrance, *"Energy Booster" Fragrance #1650076*	0.50
14. Citric Acid (50%)	1.20 (q.s. to pH 5.0)

** If a translucent system is desired, this formula may be produced without mica/TiO2, resulting in a clear product at pH 5.0.

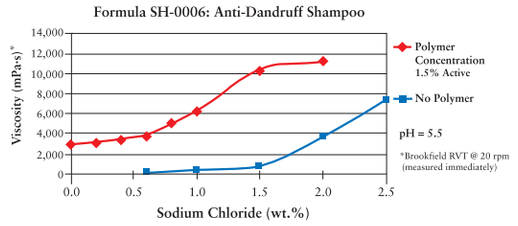
(SH-0004)

This patented 'back acid thickening' mechanism (2) can be used to further increase the efficiency of the polymer in formulation and/or to formulate products at more acidic pH. This unique feature enables the polymer to be used across a broad pH range.

Another benefit observed with Acrylates Copolymer from Noveon is synergistic thickening with surfactants and salt. Higher surfactant levels require a lower concentration of polymer to achieve the same viscosity. Maximum efficiency is realized at surfactant levels of 15-23%. Further, in the presence of surfactants, the polymer works with low levels of salt to increase viscosity (Figure 2) and yield value, unlike other Carbopol® polymers. These synergies present the opportunity for improved efficiency in use and for viscosity to be achieved using less salt, for improved mildness.

Greater electrolyte tolerance also makes the polymer ideal for use in products featuring ingredients such as botanicals and other actives.

Figure 2.



INCI Name / Trade Name	Weight %
PART A	
1. Deionized Water	39.35
2. Acrylates Copolymer (30%), *Carbopol®* Aqua SF-1 Polymer*	5.00
3. Sodium Lauryl Sulfate (29%) *Sulfochem™* SLS-WA Surfactant*	16.00
4. Sodium Laureth Sulfate (2 mole, 26%), *Sulfochem™* ES2-TK Surfactant*	16.00
5. Sodium Hydroxide (18%)	0.50 (q.s to pH 6.5)
PART B	
6. Deionized Water	10.00
7. Polyquaternium-10, *Ucare® Polymer JR-400*	0.25
8. DMDM Hydantoin	0.30
PART C	
9. Sodium Hydroxide (18%)	0.40 (q.s to pH 6.5)
10. Cocamidopropyl Betaine (35%), *Chembetaine™* C Surfactant*	4.00
11. Citric Acid (50%)	0.70 (q.s. to pH 5.5)
12. Zinc Pyrithione (48%), *Zinc Omadine FPS*	2.50
13. Dimethiconol (and) TEA-Dodecylbenzenesulfonate, *Dow Corning® 1784 Emulsion*	3.00
14. FD&C Blue No. 1 (0.1%)	1.00
15. Fragrance, *Lavender-Mint, #6550083*	0.50
16. Sodium Chloride	0.50 (q.s. to 3,500 mPa·s)

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Figure 3. Acrylates Copolymer allows insoluble agents to be suspended without sacrifycing clarity.

In the past, it proved difficult to produce a truly high clarity surfactant-based formulation with exceptional suspension properties. The three-dimensional structuring network provided by Acrylates Copolymer enables formulators to suspend beads, exfoliating agents and other insoluble agents without sacrificing the clarity of the formulation (Figure 3). Optimal clarity can be achieved at approximately pH 6.5.

The high suspending and stabilizing capacity conferred by the polymer enables exceptional shelf stability in formulations with insoluble and difficult-to-stabilize ingredients such as ZPT, silicones and other oils, and pearlizing agents.

Enhancing the 'shelf presence' of the product at point of sale is a consumer relevant benefit. Often, however, appearance modifiers such as mica, glycol stearate and glycol distearate present challenges in product stability or in providing a uniform appearance that doesn't dull or fade with time due to particle realignment. The three-dimensional structuring network of Acrylates Copolymer overcomes these issues, by stabilizing these ingredients. Additionally, the polymer noticeably improves the apparent luster and intensity of pearlescence and maintains it over time (2). This effect is most pronounced with mica (Figure 4).

Figure 4. Enhanced pearlescence in mica. The photograph shows mica in SF-1 (A) and without (D).

Recommended polymer use levels in surfactant-cleansing products are typically 5-10 wt.% as supplied (1.5-3.0% active polymer) for clear products and 5-6 wt.% (1.5-1.8% active polymer) for pearlized products. For additional versatility, rheology properties can be tailored as desired by altering the levels of various ingredients used in formulation. Table 2 gives some examples and shows expected results.

Table 2.

Factor	When factor is	Suspending and viscosity properties
Polymer concentration	↑	↑
Surfactant concentration	↑	↑
Low pH ('Back acid thickening' technique)	Utilized	↑
Salt	Added	↑
Other ingredients (EGDS, etc)	Added	Vary

Order of addition is very important in obtaining optimal benefit from the polymer. While the final order of addition may vary depending on the composition and the concentration of individual materials, the following general guidelines should be observed:

1. Add Acrylates Copolymer to the (deionized) available water of the formulation.
2. Add primary surfactants (example: lauryl sulfates, lauryl ether sulfates).
3. Neutralize to pH 6.5.
4. Add remaining surfactants (example: amphoterics).
5. Add conditioning and ancillary ingredients (example: silicones, cationics, EDTA).
6. If desired, add pearlizing ingredients (example: mica, EGDS, EGMS).
7. Add fragrance, dyes and preservatives.
8. If desired, decrease pH through 'back acid thickening' process, to increase efficiency. Citric acid is suggested.
9. If desired, add sodium chloride to further increase viscosity.

Acrylates Copolymer from Noveon can also be used for

post-thickening. The best process for post-thickening is to dilute at a ratio of 1:2 (polymer:water) and add this dispersion very slowly to the batch. This avoids forming lumps due to localized thickening with surfactants and concentrated polymer levels.

The polymer displays classic shear-thinning behavior. At low shear rates, viscosity and yield value are high and suspended and insoluble ingredients can be stabilized. At high shear rates, viscosity is low and product can easily be pumped or dispensed. Further, the polymer does not degrade under high shear agitation. Viscosity recovers immediately as shear is decreased. This translates into smooth, pourable products with high yield value and superior aesthetics.

Acrylates Copolymer is compatible with virtually all commercial nonionic, anionic and amphoteric surfactants as well as a wide array of popular additives and conditioning agents, such as widely used silicones and cationic polymers including guar hydroxypropyl trimonium chloride, polyquaternium-4, -7, -10, -11, -16 and -39. Polyquaternium-11, -16 and -39 provide the best clarity in clear formulations. Additionally, Acrylates Copolymer displays good compatibility with cationic hair dyes in surfactant-based formulations, and the polymer shows stability in acidic systems containing hydrogen peroxide at pH 2.5 - 4.0.

Acrylates/C10-30 Alkyl Acrylate Crosspolymer

Carbopol® Ultrez 20 polymer (INCI: Acrylates/C10-30 Alkyl Acrylate Crosspolymer) is a hydrophobically-modified, crosslinked, polyacrylate polymer supplied as a fluffy, white powder.

As supplied, the polymer molecules are coiled and impart relatively little suspension and viscosity. Upon neutralization, the molecules ionize and expand due to charge repulsion, and provide suspending and thickening properties to the aqueous system in which they are present. In this hydrodynamic thickening mechanism, it is primarily the physical packing ('space filling mechanism') of polymer molecules that is responsible for the development of viscosity and suspending capability. This is distinctly different from associative thickening.

Acrylates/C10-30 Alkyl Acrylate Crosspolymer provides the user with consistent dispersion viscosity and efficient thickening. The polymer features patented self-wetting technology, so it wets and disperses quickly, without requiring agitation. In ambient temperature, even at very high concentration, wetting typically takes less than 10 minutes (3). This offers a significant reduction in processing time and energy consumption compared to traditional carbomers. Recommended dispersion temperature is 25 - 50°C. The product can be dispersed at concentrations up to 6.0 wt% and still remain pumpable.

Figure 5.

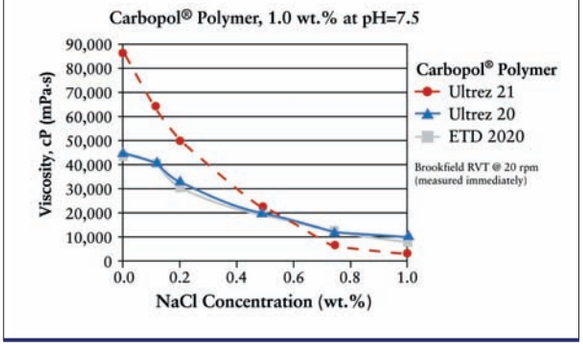
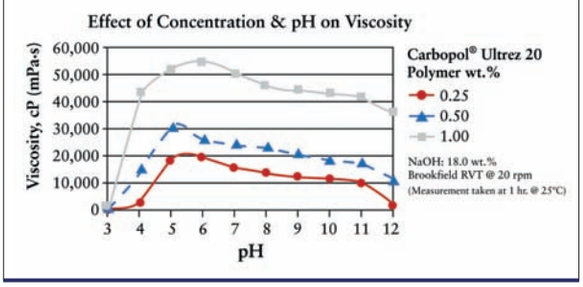


Figure 6.



Acrylates/C10-30 Alkyl Acrylate Crosspolymer maintains its integrity in the presence of electrolytes, enabling formulation with a wide range of active ingredients and additives (Figure 5).

The polymer is suitable for use in medium-to-high viscosity formulations, which demand superior appearance, smooth flow (shear-thinning) and suspending or stabilizing properties. Further, the polymer delivers effective performance across a broad pH range (Figure 6), with greatest viscosity efficiency at pH 5.0. This, along with broad compatibility with typically used cosmetic ingredients, makes it ideal for use in hair and skin care applications. Exceptional clarity is attained, even at high use levels.

In gels and emulsions, the polymer contributes to a smooth, glossy appearance – not a grainy or 'orange peel' appearance, which can signal inferior quality. Further, the polymer imparts a light, cushiony feel in applications, helping to promote an enhanced tactile experience in use. In creams

and lotions, the polymer can be used for co-emulsification. In addition, improved wet combing has been observed in hair care applications formulated with Acrylates/C10-30 Alkyl Acrylate Crosspolymer.

Recommended polymer use level is formulation dependent. For surfactant-cleansing applications with low-to-moderate surfactant actives (<12 wt.%), 0.8 - 1.0% is recommended. For use in emulsions and gels, 0.3 - 0.7% is recommended, depending on electrolyte content.

Processing instructions are simple.

1 Sprinkle polymer on surface of water and allow to self-wet.
2 Begin gentle agitation.
3 Keep agitation to a minimum (to avoid air entrapment) while adding remaining ingredients to formulation.
4 Neutralize: can be pre- or post-neutralized (depending on the needs of the formulation).

Polyacrylate-14

A third new technology from Noveon is Polyacrylate-14, designed to improve hair style longevity while enhancing sensory and aesthetic properties, both in formulation and in use. Fixate® PLUS polymer (INCI: Polyacrylate-14) is a unique, multi-functional polymer that delivers film-forming, fixative *plus* rheology modifying properties in formulations.

Typical properties, as supplied, are shown in Table 3:

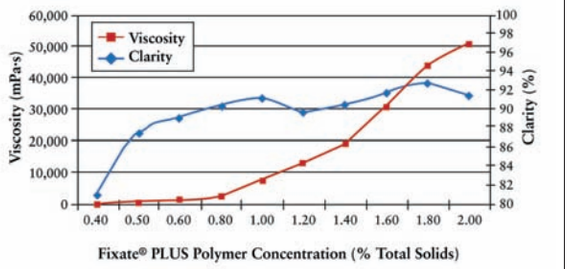
Table 3.

Appearance	Milky white liquid
Viscosity (mPa·s)	15
Active polymer (% by weight)	30
pH	3.0

The patent-pending design of this alkali-swellable associative polymer (ASAP) combines hard hydrophilic, soft hydrophobic and semi-hydrophobic components to deliver an optimized balance of properties. This novel combination leads to excellent hold and good solubility; clear, uniform films with good adhesion; superior humidity resistance and a smooth, natural feel on hair.

Traditional hydrophobic associative polymers, particularly those with long chain hydrophobes, can build very strong hydrophobic associations in solution. The resulting gels can be highly thixotropic, with poor texture and appearance in the presence of shear stress. In contrast, the semi-hydrophobic pendants in the structure of Polyacrylate-14 enable controlled hydrophobic association, improving thickening efficiency, while maintaining the smooth, buttery feel and classic shear-thinning rheology characteristic of gels formulated with Carbopol® polymers.

Figure 7.



When neutralized with a base, the polymer opens and develops viscosity with high clarity at approximately pH 6.5. At 1.0% active polymer, viscosity reaches 7,000 mPa·s, with viscosity increasing rapidly as concentration is increased, while maintaining high clarity (6) (Figure 7).

Due to its hydrophobic modification, Polyacrylate-14 offers exceptional efficiency with hydrophobically-modified carbomer copolymers (such as Carbopol® Ultrez 20 or Ultrez 21, INCI: Acrylates/C10-30 Alkyl Acrylate Crosspolymer) due to association between the hydrophobic groups. Again, clarity in formulations is very high.

As a liquid polymer, Polyacrylate-14 offers simplicity in processing.

1 Disperse desired thickener (Carbopol® polymer recommended) in deionized water and allow to wet/hydrate according to manufacturer's instructions.
2 Using gentle agitation, slowly add Polyacrylate-14 polymer. Mix until homogeneous.
3 Combine desired additives; add to dispersion using moderate agitation.
4 Neutralize to desired pH and clarity (recommended >6.5 for best clarity).

As noted, Polyacrylate-14 is a multi-functional polymer. Even at low use levels, Polyacrylate-14 provides fixative properties with exceptional high humidity curl retention

Figure 8.

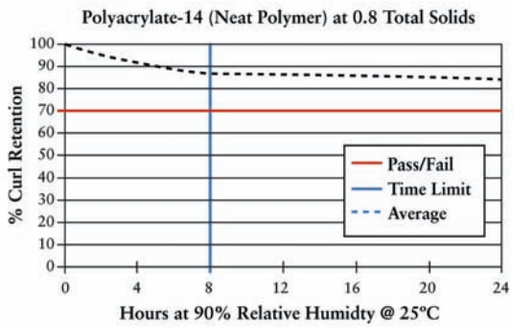


Figure 9.

(HHCR), whether used alone (Figure 8) or when used in combination with leading rheology modifiers.

In laboratory evaluations, styling gels formulated with just 1.0 wt% total solids (0.5 wt% Polyacrylate-14 with 0.5 wt% Acrylates/C10-30 Alkyl Acrylate Crosspolymer (4)) demonstrated greater than 90% curl retention after 24 hours at 90% relative humidity (RH), 25°C. Figure 9 shows the curled tresses after 24 hours.

In qualitative salon tests, styling gels formulated with 0.8 wt% Polyacrylate-14 and 0.2 wt% Carbomer (5,7) were observed to impart greater fullness and body, without stickiness or heaviness, when compared to a commercial styling gel formulated with PVP. Figures 10, 11 and 12 demonstrate these results.

Polyacrylate-14 offers 'weightless', touchable hold at low use levels (0.5 - 1.0% active polymer), though commercial formulations have been developed using this polymer as the sole rheology and fixative agent (at use levels of 2.0 - 3.0% active polymer) in products positioned for firmer hold. For added 'crispness' in styling applications,

Figure 10.

Side styled with styling gel formulated with Polyacrylate-14

Figure 11.

Side styled with commercial styling gel formulated with PVP

Figure 12.

Left side styled with PVP
Right side styled with Polyacrylate -14

Polyacrylate-14 can be mixed with AMP-Acrylates/Allyl Methacrylate Copolymer (Fixate® G-100 polymer, from Noveon) with the interesting synergy of providing higher 'crispness' than either polymer can offer individually. Alternately, Polyacrylate-14 can be mixed with traditional polymers, such as PVP or PVP/VA. By balancing use levels, the poor humidity resistance of these traditional polymers can be enhanced due to the superior humidity resistance offered by Polyacrylate-14.

Conclusions

The quest for product innovation and differentiation demands new technology that can empower formulators to develop new, exciting applications that delight the consumer – both functionally and through the senses. By providing multi-functionality and exceptional sensory properties, Acrylates Copolymer, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, and Polyacrylate-14, all from Noveon, break the boundaries of traditional rheology modifier performance, enabling formulators to create products which can exceed consumers' expectations. These polymers enable versatility in formulation while providing efficiency essential to managing cost constraints.

References

1. Carbopol® Aqua SF1 polymer (INCI: Acrylates Copolymer), Carbopol® Ultrez 20 polymer (INCI: Acrylates/C10-30 Alkyl Acrylate Crosspolymer) and Fixate® PLUS polymer (INCI: Polyacrylate-14) are trademarked products of Noveon, Inc., a wholly owned subsidiary of The Lubrizol Corporation. Trademarks are owned by The Lubrizol Corporation.
2. US patents 6767878 and 6897253
3. Carbopol® Ultrez 20 polymer product specification for 3.0% active polymer: wetting time maximum 10 minutes, dispersion viscosity >3,500 mPa· s (20 rpm, 25°C) after 3 hours.

4. Carbopol® Ultrez 21 polymer
5. Carbopol® 980 polymer
6. Fixate® PLUS polymer product specification for 1.0% Gel: 1.0% wt. polymer solids in water, neutralized with AMP-95® to pH 6.8 – 7.2, measured at 24 hr: viscosity minimum 7,000 (mPa·s) with clarity >90%T.
7. Styling gel starting formulation S-G0015 (FP-0001) can be referenced at www.personalcare.noveon.com

Further information

For more information, samples and/or starting formulations (including those shown in the content of this article) with complete processing instructions and supplier references, please contact Noveon, 9911 Brecksville Road, Cleveland, Ohio 44141-3247, 800-379-5389 or 216-447-5000; contact your Noveon representative or visit www.personalcare.noveon.com

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