New polymer technology

Bimodal polymers enable lower VOC formulating possibilities.

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Regulatory legislation and environmentally-focused consumer groups continue to challenge the personal care industry to reformulate aerosol hair styling aids in an effort to lower the levels of volatile organic compounds. The industry has contested that there may not be sufficient technology to permit the formulation of marketable aerosolized products that would deliver performance attributes economically, aesthetically, and safely. This paper introduces a new polymer technology that can help to bridge such gaps.

Consumers expect a number of often contradictory properties from hair styling sprays, yet the ultimate goal is the same: the uniform application of a clear polymeric material to the hair to achieve certain improvements in appearance and manageability. The hair style must be held firmly in place under conditions of high temperature and humidity, yet the hair must not feel too stiff. The spray dispersion must be fine enough to avoid nozzle clogging and sputtering, yet not pose an acute inhalation risk. The formula must contain enough non-VOC components to meet regulatory requirements; however, if it is an aqueous-based formula, it must dry quickly after application. The resin solution must be able to flow along the hair shaft to help promote adherence to the adjacent hair fiber as the polymer dries, but not create flakes during subsequent brushing or combing when either wet or dry. The hair must appear natural and glossy, but not feel tacky or sticky, even under conditions of high humidity. Finally, the fixative polymer must be long-lasting, yet readily removable from the hair during subsequent shampoo applications.

Acrylic copolymer technologies offer an alternative approach to traditional polymers such as PVP, PVP/VA and other high molecular weight copolymers. Interpolymer recently developed an innovative technology identified as "Bimodal." This refers to its structure, which is composed of two different types of acrylic polymer molecules: one with an ionic and the other one with cationic functionalities (patent-pending). The unique bimodal technology was designed to enhance hair styling products by improving hold performance in quick-setting, low VOC aqueous-based formulations.

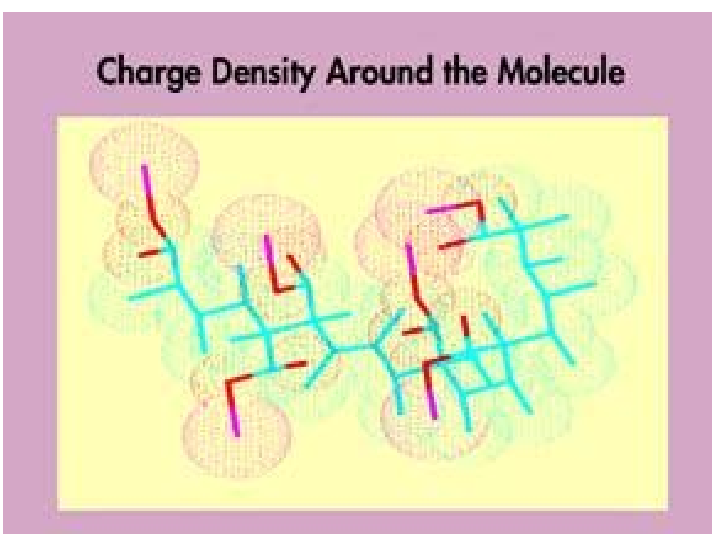


Figure 1: Charge density around one chain of acrylic copolymer. Interpolymer Lab Presentation using HyperChem® 7.

Bimodal Polymers: Structural Properties

The bimodal technology is designed to enhance hair styling products by improving "hold performance." These properties are accomplished through an innovative technology that uses a bimodal interpenetrating network, which simultaneously delivers both cationic and anionic polymers to the hair shaft. The result is a reversible, cross-linked polymer complex achieved by the ionic associations of the two oppositely charged polymer chains, which provide both excellent holding power and ease of removal. The anionic chain is designed to contribute to the polymer's removal properties, while the cationic chain imparts strong hold and ease of styling. The ionic combination of the two oppositely charged polymer chains during drying allows the bimodal polymer to mimic the functions of higher molecular weight polymers. This combination of lower molecular weight and high charge density allows the bimodal polymers to be easily sprayed and yield adequate hold when applied. The bimodal polymers have film formation temperatures that are balanced to give a pleasant feel without flaking.

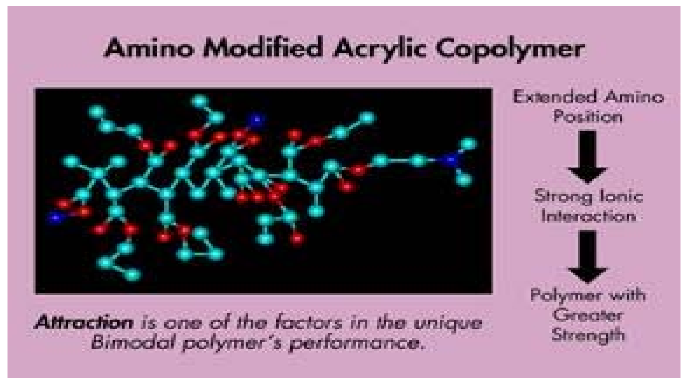


Figure 2: Amino modified acrylic copolymer, Interpolymer Lab Presentation using HyperChem® 7.

Figure 1 illustrates the importance of the charge density around one chain of an acrylic copolymer. It demonstrates the strong ionic association that can be formed when two or more chains associate to form an interpenetrating network. The amino function is placed in an exposed position to interact with the acidic part of the anionic acrylic copolymer chain to form an interpenetrating network (Figure 2). Co-monomer

Formula 1
Low VOC Aerosol Bulk Concentrate

Phase A	INCI Designation	Weight %
	Alcohol Denature	70.00
	Aminomethyl Propanol	0.50
	PEG-12, Dimethicone	0.10
	PEG-45 Palm Kernel Glycerides	0.05
Phase B	Polyacrylates-18 (and) Polyacrylates-19 (Interpolymer’s Syntran® 5117)	19.35
	Ammonium Acrylates Copolymer	10.00
	Yield:	100.00

Procedure:
Add ingredients to appropriate vessel as listed. Stir between each addition until batch is clear and homogenous. Adjust pH to 8.4-8.8 with AMP-95 at end; stir until homogenous. Product is a slightly turbid solution.

Final Formula:

35% VOC	Bulk Concentrate	50.00
	Hydrofluorocarbon 152A	50.00
	Yield:	100.00
55% VOC	Bulk Concentrate	63.00
	Dimethyl Ether	10.50
	Hydrofluorocarbon 152A	26.50
	Yield:	100.00

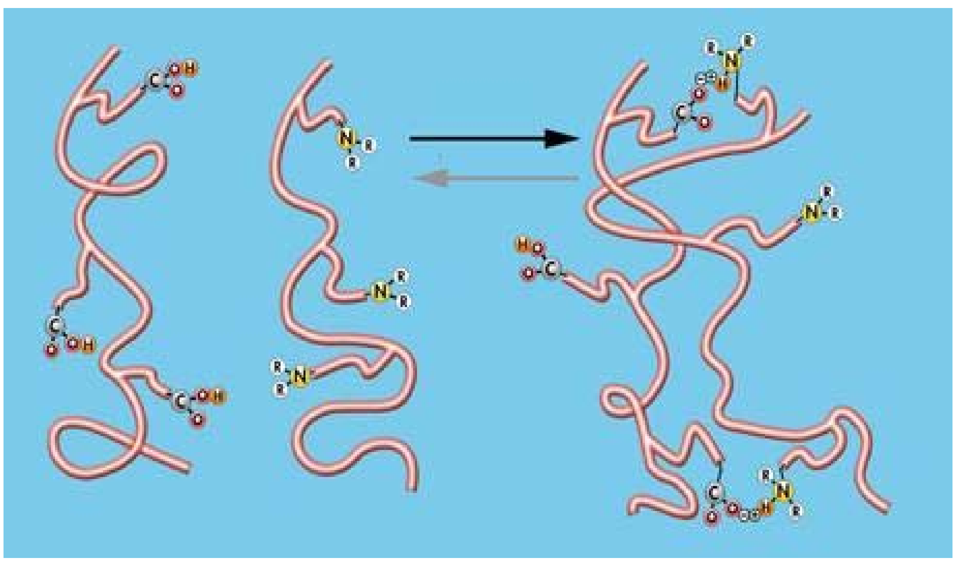


Figure 3: Illustration of the ionic bonding of Bimodal Syntran Polymers.

selection and molecular weight control allow Interpolymer to optimize the steric hindrances and ionic interactions, which result in specific setting and hold properties. Polymer composition plays an important role in this geometrical and electrical interaction.

The inclusion of strongly electropositive or electronegative groups on separate molecules causes an inductive shift of electrons. This shift plays an important role in the polymer’s cohesive and adhesive properties. Since the bimodal polymers are composed of both electropositive and electronegative groups, there is significant potential for the polymer chains to exhibit this shift in electron density. At large distances, these polymer chains would behave like an electrically netural system. However, as the ionic groups are brought into close proximity to their counter-ion during the drying process, strong secondary bond forces begin to exert their influence and give the bimodal polymers their unique characteristics. Figure 3 illustrates the ionic interaction during the drying process.

This novel technology relies on the ability to produce stable dispersions and solutions containing polymer molecules with different ionic changes. During the drying process, the bimodal polymer will form an ionic complex, as described above, even before the final film is completely dry and sets on the hair.

The resultant polymer complex prevents the formulation from migrating even before the water or solvent has completely evaporated. Because bimodal polymers set quickly under high humidity conditions, they can provide a reliable alternative to current hair care polymers.

Bimodal polymers in very low VOC aerosols

Bimodal polymers were incorporated into aerosol sprays in an effort to determine if an aqueous based 35% VOC formula could deliver a comparable performance to existing brand name 55% VOC hair sprays. An additional resin was incorporated into the control formula to assist with ancillary benefits, such as gloss and lustre. The control formula is show in Formula 1.

High humidity curl retention test

A curl retention study was conducted to determine the efficacy of the bimodal technology in 35% and 55% low VOC aerosol hair sprays. Materials chosen for this evaluation were the Polyacrylate 18 (and) Polyacrylate 19 bimodal (Interpolymer’s Syntran® 5117) and the Ammonium Acrylates Copolymer as stipulated in Formula 1.

Method

Virgin hair tresses from International Hair Imports were washed with a consumer available shampoo (KPAK Reconstruct from Zotos) per the instructions found on the bottle. The hair swatches were made of black Chinese hair swatched in 4 gram clips (combined hair and clip weight) which were 17.8 cm in length (hair only). Hair swatches were then divided into four groups of two each for evaluation. The materials evaluated were:

1) Control formula @ 35% VOC (50 g concentrate/50 g 152A)
2) Control formula @ 55% VOC (63 g concentrate/10.5g DME and 26.5% 152A)
3) Major brand with flexible hold (Labeled as containing no CFCs but no mention of CAS compliance)*.

*[Ingredients Listed in the Major Brand: Water, SD alcohol 40B, dimethylether, hydrofluorocarbon 152A, VA/Crotonates/Vinyl Neodecanoate Copolymer, Acrylates/Hydroxyesters Acrylates Copolymer, Fragrance, aminomethyl propanol, sodium benzoate, cyclohexylamine, dimethicone colpolyol, cyclopentasiloxane, silk amino acids (list of nine), Borago Officinalis Seel Oil [Palmitic acid, Steric Acid, Linoleic Acid, Oleic Acid, Eicosenoic Acid], Glycerin.]

Two swatches of hair were prepared for each spray. After curling and spraying, the swatches were divided into humidity test group and ambient test group and evaluated for a period of four hours.

Table 1: Hair Lengths / Curl Retention					
Sample	**Original Curl**	**One Hour**	**Two Hours**	**Three Hours**	**Four Hours**
Room Temp					
35% Control	14.5	15.5 / 69.7	15.0 / 84.8	15.0 / 84.8	15.3 / 75.8
55% Control	14.0	15.0 / 73.7	14.5 / 86.8	14.5 / 86.8	14.5 / 86.8
Major Brand	12.5	14.0 / 71.7	13.5 / 81.1	13.5 / 81.1	13.8 / 75.5
Humidity					
35% Control	14.0	15.0 / 73.7	15.9 / 50.0	15.7 / 55.3	16.0 / 47.4
55% Control	13.5	14.5 / 76.7	15.0 / 65.1	15.0 / 65.1	15.5 / 53.5
Major Brands	12.5	14.0 / 71.7	14.7 / 58.5	14.7 / 58.5	14.7 / 58.5

$$\text{Curl Retention} = \frac{\text{Original hair length} - \text{Test curl length}}{\text{Original hair length} - \text{Original curl length}} \times 100$$

Procedure

Two swatches for each spray were prepared by washing with a commercial shampoo per manufacturer's instructions and blown dry using a standard consumer hand-held hair dryer set on a low setting. To insure that the swatches were dry, they were placed in a 38^{o}C circulating air oven for 10 minutes before styling. The swatches were then curled before styling with a consumer grade curling iron set on its highest setting. Swatches were held in the iron for 45 seconds to set the curl. When the swatch was removed, it was placed immediately on its side while the second curl for the same test spray was prepared. After both swatches were prepared and still lying on their sides, the test spray was applied by spraying each swatch with approximately a one second burst of hair spray. The swatches were then flipped and then sprayed again on the opposite side. This was done for each spray. The swatches were allowed to dry for five minutes before moving into a vertical position for measurement. Before the tresses were measured, each received another one second application of spray while in the vertical position and allowed to dry.

The swatches were divided into the test groups and hung for evaluation. Ambient conditions were 74^{o} F/45% RH and humidity conditions were 84^{o} F/95% RH. Curl length was determined as a function of time.

Percent Curl Retention was calculated by means of the following equation:

% Curl Retention = 100 x [(L - L_t) / (L—L_0)] where:

L = length of hair fully extended (before curling)

L_0 = length of curled hair before exposure

L_t = length of curled hair after exposure as a function of time.

Results

Table 1 lists the test results from this evaluation for a period of four hours.

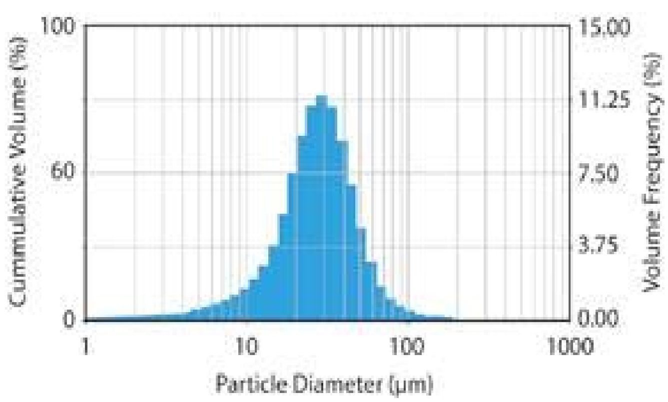
One variable not measured in this study was the amount of polymer deposited on the hair while spraying. The major brand's formula was not tested for total solids content, and we can assume that it also perhaps contained a greater amount of polymer solids. The control formulations, on the other hand, did not have the heavy, wet appearance or feel. The control formulation spray patterns were similar to the major brand product. As a proof of concept study for 35% VOC sprays, this appears to indicate that there is validity to the claim that bimodal polymers offer improved technology in low VOC applications.

Dispersion / Packaging

On March 2, 2005, several cans of the control 35% VOC formula were filled at Precision Valve in Yonkers, NY in an effort to establish optimum valve specifications, measure average particle size distribution, and generally assess the formulation's performance.

The preferred valve specifications for this formula were deemed to be:

020 MB Concave Kosmos
016 S90
Buna N S90
018 X 013 S90
Alum, Epon T/B, Cut Gasket



The average particle size distribution using the Insitec Measurement System was roughly 30 microns of which specifically:

Dv (90) = 50.33 (mm) D[4][3] = 30.18 (mm)

After initial filling of canisters, a pressure rating of 63 psi at room temperature and 127 psi at 130^{o} F was observed. In addition, a delivery rate of 0.78 grams/second was determined with a spray pattern at 8 inches providing a 3 inch diameter circle.

Safety/toxicity

Because the large molecular size of this polymer limits its bioavailability and none of the components are considered to be acutely hazardous, little or no systemic toxicity would be expected by the oral, dermal and inhalation routes of exposure. The airborne particle size distribution of this product after spraying from an aerosol can was evaluated. The aerosol formulation consisted by weight of approximately 19% concentrate, 91% of which was Polyacrylate 18 (and) Polyacrylate 19, and approximately 81% solvent/propellant. The mean aerosol particle diameter was 45.1 µm and approximately 95% of the particles had a diameter greater than 10 µm. Since particles with diameters greater than 10 µm are not respirable to humans, similar aerosol formulations of Polyacrylate 18 (and) Polyacrylate 19 (Interpolymer's Syntran® 5117) do not pose an acute inhalation hazard.

A topical application ocular irritation screening assay using the EpiOcular™ human cell construct was conducted using the dry form of the polymer to evaluate the potential toxicity of the test article for various exposure times (1, 2, 4, 8 and 24 hours). The duration of exposure resulting in a 50% decrease in 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) conversion in test article-treated EpiOcular™ human cell constructs, relative to control cultures, was determined (ET50). This study resulted in an ET50 value of 3.3 hours, with 15.2% cell viability at the 24-hour exposure period. Based on the results of this study, this product is classified as non-irritating to the eye (IIVS, 2004_a).

A topical application ocular irritation screening assay using the EpiOcular™ human cell construct was conducted using the wet form of the polymer to evaluate the potential toxicity of the test article for various exposure times (2, 4, 8, 16 and 24 hours). The duration of exposure resulting in a 50% decrease MTT conversion in test article-treated EpiOcular™ human cell constructs, relative to control cultures, was determined (ET50). This study resulted in an ET50 value of 6.3 hours, with 10.9% cell viability at the 24-hour exposure period. Based on the results of this study, this product is classified as non-irritating to the eye (IIVS, 2004b).

The lack of ocular irritation potential established by the ET50 values also indicates that the product is not likely to produce dermal irritation or sensitization, since skin is less susceptible to irritation than eye tissue. In addition, a human repeated insult patch test (HRIPT) was conducted with the closely-related product, another bimodal polymer, in 100 male and female volunteer subjects to evaluate skin sensitization potential definitely. Observations throughout the test interval were within normal limits; therefore, it may be concluded that this product, as well as Polyacrylate 18 (and) Polyacrylate 19 (Interpolymer's Syntran® 5117), would not produce allergic contact sensitization following repetitive dermal exposure (CPTC, 2005).

Genetic toxicity profile

A reverse mutation using the direct plate incorporation method was conducted with this product in *Salmonella typhimurium* strains TA98, TA100, TA1535 and TA1537 and *Escherichia coli* WP2 uvrA, both with and without metabolic activation. The dose levels tested were 1.5, 5.0, 15, 50, 150, 500, 1500, and 5000 µg per plate. Results were negative in the mutagenicity and confirmatory tests for this product under the conditions of the bacterial reverse mutation assay both with and without metabolic activation (BioReliance, 2005).

Conclusion

This novel bimodal polymer technology is based on unique, interpenetrating polymer networks. By incorporating both cationic and anionic functionalities, the bimodal polymers offer a formulator the opportunity to create alternative very low or low VOC aqueous-based hair sprays.

The test data indicate the bimodal polymers can provide good high humidity curl retention and can set quickly. Furthermore, due to the molecular weight of these polymers, formulators can deliver excellent dispersion patterns and particle size distributions. Finally, the polymers exhibit good aesthetic characteristics when evaluated on wet and dried hair. This versatility makes them a reliable alternative to current hair care polymers and for the next generation of lower VOC hair styling products.

For more information, visit www.interpolymer.com.