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Characterization of hair styling formulations targeted to specific multicultural needs

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Synopsis

The ethnic hair care market is large and diverse, with many unmet needs, especially when the definition of ethnic varies as much as the hair does. By examining the variety of hair care raw materials now available, we designed hair styling formulations for targeted benefits such as anti-frizz, conditioning, style control, humidity resistance, UV protection and color loss protection. We have characterized three distinctive hair styling formulations targeted to specific multicultural needs. This has been completed by using standard personal care laboratory evaluations including the Diastron Limited ™Miniature Tensile Tester for stiffness, the Bossa Nova Technologies ™ Shine Instrument, high-humidity curl control, UV exposure, and expert panel evaluations; the results were substantiated using current state-of-the-art analytical tools, including atomic force microscopy and scanning electron microscopy. Results demonstrate that a varied product portfolio is required for such a diverse market segment. Styling products ranging from alcoholic sprays, leave on styling creams or gels and styling curl activators offer performance attributes that can be utilized on a variety of hair types such as Asian, African, Caucasian and Brazilian.

INTRODUCTION

Film forming polymers and cationic conditioning agents offer improved luster, style/humidity control, anti frizz and conditioned feel on many types of multicultural hair, including: African, Asian, Caucasian, and Brazilian hair. African hair is most difficult to control because the hair shaft is shaped like a flattened oval and will self-curl or coil on itself. Brazilian hair is a mixture of hair types that is wavy in nature and reflects the diverse ethnicity of much of the population in the Americas. Asian hair is cylindrical and the most challenging to curl. See Figures 1a, b, c, and d. Not only are there variations of hair based on ethnicity, but other hair variations exist such as, along a single strand, from strand to strand ,and the hair experience: UV exposure, color dyeing, bleaching, perming, relaxing, heat tools, and mechanical damage.

Formulating for a variety of enhanced attributes on a variety of ethnic hair types can be achieved by the use of acrylates/hydroxyesters acrylates copolymer for enhanced shine, flaking resistance, humidity and style control; zinc oxide and simmondsia chinensis (jojoba) seed oil and glyceryl stearate and polyhydroxystearic acid (to be referred to as zinc oxide and jojoba oil) for color protection, feel and anti-frizz control; polyquaternium-10

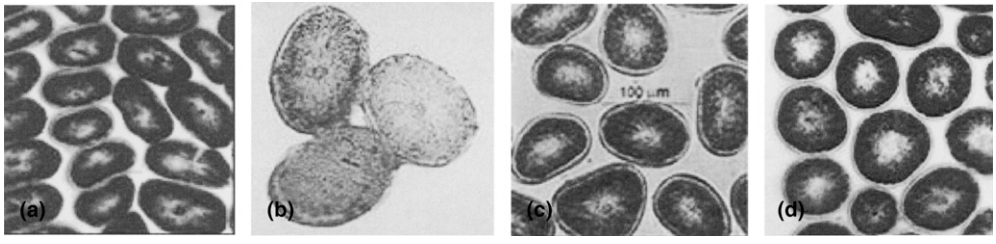

Figure 1. (a) African oval-flat shape moderate diameter. (b) Caucasian semi-oval elliptical fine/moderate diameter. (c) Latin semi-oval elliptical fine/moderate diameter. (d) Asian round to circular large diameter.

and polyquaternium-67 for ease of combing, feel, and manageability; acrylates/steareth-20 methacrylate crosspolymer for rheological properties, enhanced style control and high humidity resistance. Treatment of African or Brazilian hair tresses; as well as Caucasian or Asian hair types; with styling treatments based on these products provide excellent anti-frizz control compared to silicones and maintain overall control under humid conditions.

Intensive testing indicates, depending on the hair type, that changes in the styling benefits and attributes can be delivered for a natural, not coated feel with different formulations. Characterization of these prototype formulations was completed by using a variety of methods—from expert panelists, curl stiffness, UV damage, color loss protection, and humidity testing to highly sophisticated analytical tools including SEM morphology and elemental mapping and AFM.

EXPERIMENTAL METHODS

Our experiments involve the use of standard personal care methods as well as state of the art analytical tools. These are described in this section.

DIASTRON CYCLIC COMPRESSION: STIFFNESS RETENTION

- Pretreatment: The hair tresses (European Brown Virgin Hair, obtained from International Hair Importers, New York) prior to curling were on the average 8 inches long and weighed 3.5±0.1 grams. They were washed in mild shampoo before using and curled wet onto a 22 millimeter (mm) × 70 mm curler and held in place with a bobby pin. The curled tresses were allowed to dry on the lab bench overnight.
- The curled tresses were uniformly sprayed twice in the front and twice on the back from a distance of 20.3 centimeters (cm) with the hair spray formulation. The spray device dispensed 190 µl (micro liters) of formulation with each compression. The spray device product was "Euromist Classic™" and was manufactured by SeaquistPerfect, Cary, IL. The curled, treated tresses were dried for 1 hour in a controlled environment at 22.5°C and 55% relative humidity. The curler was removed carefully without uncurling the tress. The curled tress was placed in the miniature tensile tester, model MTT160 instrument (Diastron Limited, Unit 9 Focus 303 Business Centre, Andover, Hampshire SP10 5NY UK, or 390 Reed Road, Broomall, PA 19008, USA) and the work to compress the curl to 50% of its initial diameter was measured. The compression was repeated five

times for each tress. Measurements were made at about 22.5°C and 55% relative humidity. The percent stiffness retention was determined by the following equation:

$$\% \text{ stiffness retention} = (w_5/w_i) \times 100,$$

where wi is the work of the first compression and w5 is the work needed to compress the curl on the fifth consecutive compression. In this test, good stiffness retention is taken to be a measure of good durability on the hair.

HIGH-HUMIDITY CURL RETENTION TEST

Curled tresses were prepared and treated as in the DiastronTM curl compression test above. After drying, the curlers were gently removed from each tress and curls were suspended by clips in a humidity chamber at room temperature and approx. 90% relative humidity. Initial curl length was recorded. The length of the curled tresses was recorded at intervals over 4 h. Curl retention is determined as [(L (0)-L(t))/L(0)-L(i))×100] where L(0) is fully extended curl length, L(i) is initial curl length and L(t) is curl length at a specific time.

ATOMIC FORCE MICROSCOPY

For the AFM analysis, samples of hair were removed from the tresses approximately 3-4 cm from the binding at the root end. One to two inch pieces of cut hair was then glued to a glass slide using "fast dry" liquid paper. One set of images consisting of a 20 um and 100 um were obtained from each hair. Three hairs were imaged from each tress. Images of the sample surfaces were obtained using a Bruker D 5000 AFM (Bruker, Santa Barbara, CA) and an OTESP tip (Bruker) operated in a conventional mode with height images being collected. Subsequent image analysis was determined using a SPIPTM software package.

SCANNING ELECTRON MICROSCOPY: MORPHOLOGY & ELEMENT MAPPING

- The samples were mounted on an Al plate and Au/Pd coated for 60 sec. SEM images were collected with the Hitachi S-3400N VP-SEM, at an accelerating voltage of 15.0 KeV, a probe current setting of ~65, and a chamber pressure of 15 Pa. X-Ray maps were collected under the same operating conditions with the Thermo Noran SD detector for 200 sec.
- There are two contrast mechanisms in the SEM: edge contrast (where sharp edges appear bright) and atomic number contrast (where species of higher atomic number appear brighter than those of lower atomic number).

RESULTS AND DISCUSSION

AFM RESULTS FOR ENHANCED SHINE

Images were taken of untreated Caucasian, African, and Latin hair using the AFM and initial surface roughness values were obtained using the SPIP™ image analysis software.

We then treated the same identical hair shaft with acrylates/hydroxyesters acrylates copolymer from a 55% VOC pump formulation hair spray, and reanalyzed each hair and determined the average surface roughness (Ra). In each case a noticeable decrease in surface roughness was obtained.

We have found that across a broad range of hair types we have the average roughness has decreased; from 87% for Caucasian hair, 35% for African hair, and 31% for Latin hair. The decrease in roughness directly equates to increased smoothness on the individual hair shaft. The acrylates/hydroxyesters acrylates copolymer hair fixatives are very effective at creating a smoother surface and hence enhancing shine on a micro level on individual hair shafts. The data indicates that Caucasian hair types responded best to alcoholic sprays for enhanced shine and styling benefits, although benefits are achieved across all hair types tested (see Table I).

Here we have images of Caucasian hair; before treatment and after application of acrylates/hydroxyesters acrylates copolymer from a 55% VOC spray. We can clearly see the ridges of the cuticles before the application of the hair spray and after treatment we observe much less roughness, or increased smoothness (see Figures 2a and 2b).

The AFM measurement was taken along a 100-micron length of the hair shaft which provides 10-20 cuticles in the image. The instrument moves a fine tip over the hair cuticle and measures the changes in height or topography or overall surface. The brighter feature in the image, the higher it is with respect to its surroundings. For example, in Figure 2a the cuticle edges are higher than the surrounding area, so the cuticle edges are brighter in the image. When the individual cuticles have been flattened or the cuticles have been filled in after treatment the edges are more difficult to see. The difference between the cuticle edge and the surrounding area is much less. Now the difference in the edge and the surrounding area is less, the overall surface roughness has been reduced.

Table I
Surface Roughness Reduction Across a Variety of Hair Types, Confirmed by AFM Measurements

	Caucasian	African	Latin
Decrease in surface roughness as measured by AFM (average 3 measurements)	87% ± 9.3	35% ± 5.9	31% ± 5.6

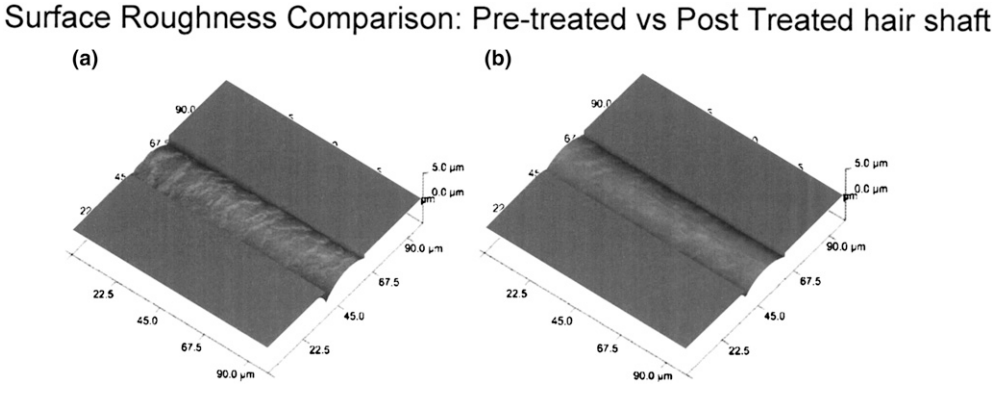

Figure 2. (a) Pre-treated hair shaft. (b) Post-treated hair shaft.

With the reduction in roughness there is a smoother surface, which correlates to an improvement in shine. Again this benefit was observed across a variety of hair types where the cuticles were either flattened or the valleys have been filled in with the thin layer of styling and shine treatment.

ACRYLATE-BASED TECHNOLOGY RESULTS FOR HOLD AND NON-FLAKING

Not only do the acrylates/hydroxyesters acrylates copolymer hair fixatives provide enhanced shine across a variety of hair types, they also provide high humidity curl retention. Asian hair tresses were curled then treated with the acrylates/hydroxyesters acrylates copolymers 1 and 2, with the control silicone spray pictured in the middle (see Figure 3; Table II). The tresses were air dried, then exposed to a high-humidity chamber for 8 hrs at 90% relative humidity and 30°C. The acrylates/hydroxyesters acrylates copolymers were able to maintain their style retention and control while the silicone-containing product had significant loss in style control under humid conditions.

When the hairspray dries, the hair fixative creates a network of "welds," the polymer forms films between hair fibers that act to secure the hair in place. The polymer can be distributed as either spot welds, at the intersection of two fibers, or seam welds, in the space between two parallel fibers. This network of spot and seam welds are distributed in a thin layer across the hair shaft filling in the valleys to create a smooth surface that enhances shine and a bound network of fibers for enhanced hold even under humid conditions.

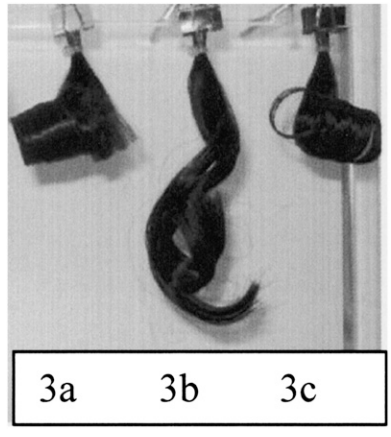

Figure 3. Asian hair: 8 hrs, 90% RH, 30°C.

Table II
% Curl Retention after 8 hrs at 90% RH and 30°C

	Initial	4 hrs	8 hrs
Fig. 3a Acrylates/hydroxyesters acrylates copolymer 1	100	95	90
Fig. 3b Commercial silicone/polymer spray	100	70	45
Fig. 3c Acrylates/hydroxyesters acrylates copolymer 2	100	90	85

Beyond a styling spray, the acrylates/hydroxyesters acrylates copolymers can be incorporated into a hair gel. The acrylates/hydroxyesters acrylates copolymers are also non-flaking as can be observed after combing through a bundle of Brazilian hair, where we compared the acrylates hair fixative to a polyvinylpyrrolidone-based hair fixative. The PVP based product has significant flaking on the hair and residue on the comb. By having a continuous 'non-flaking' film on the hair, there is a smoother, shinier surface. The PVP film tends to crack and flake, giving a discontinuous film that appears matte or dull (see Figures 4a and 4b).

The rheology modifier, acrylates/steareth-20 methacrylate crosspolymer, is used to thicken the hair gel. These are multifunctional by providing thickening and viscosity control and inherent film formation. The rheology modifiers have the ability to provide hold and style control as well as humidity resistance in clear hair gels as shown in Table III below.

ZINC OXIDE AND JOJOBA OIL RESULTS FOR COLOR PROTECTION

Zinc oxide offers broad spectrum absorption across the whole solar UV range (UVA + UVB). Traditionally, zinc oxide has been formulated into sunscreens for the sun care market. Although an effective UV filter, its lack of transparency limited its use. A new micron sized zinc oxide product in combination with jojoba oil offers opportunity to expand the use of zinc oxide beyond sunscreens and in hair care products. zinc oxide and jojoba oil deliver color protection, enhanced feel and anti-frizz control. Jojoba oil is natural product and non-greasy. It is commonly used in hair treatments, especially hair that is dry or damaged, has split ends and is prone to breakage and tangling. Jojoba is considered moisturizing oil since its molecules are small enough to penetrate the hair cuticle. Using products with jojoba oil as a hair treatment will give your hair a healthy shine and conditioned feel.

To demonstrate the attributes of zinc oxide and jojoba oil in a styling cream, bleached hair was dyed using L'Oreal Cherry Cordial™ (Manufactured by L'Oreal Group Cosmetic Company), treated with zinc oxide and jojoba oil comparable to those in a commercial control

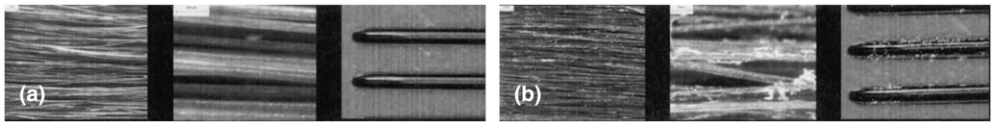

Figure 4. (a) Acrylates RM and HF hair gel. (b) Commercial hair gel.

Table III
% Curl Retention after 8 hrs at 90% RH and 30°C

	Initial	4 hrs	8 hrs
PVP/carbomer commercial hair gel (control)	100	50	10
Acrylates/steareth-20 methacrylate crosspolymer	100	75	50
Acrylates/steareth-20 methacrylate crosspolymer and acrylates/hydroxyesters acrylates copolymer	100	90	85

cream, then exposed to UV using parameters from Table IV below. After exposure the zinc oxide and jojoba oil-treated tresses had barely perceptible color loss compared to a commercial control claiming to prevent color loss, which had very distinctive and perceptible color loss (Figure 5).

AFM RESULTS FOR ZINC OXIDE AND JOJOBA OIL

Hair tresses were evaluated using atomic force microscopy before and after exposure to UV for 7 days (see Figures 6a, b, c, and d).

The hair samples were imaged by two different types of microscopy, atomic force microscopy and scanning electron microscopy. For the most part there is a great deal of overall agreement of the morphology of the hair obtained by the two techniques. Where a feature

Table IV
UV Exposure Parameters

Settings	Hair
Program 313 nm light, no water	European, bleached
Irradiance - 0.35 W/m2 @ 340 nm	Colored with Couleur Experts 6.6
Panel temp 60°C, 168 continuous hrs	Bright Autumn by L'Oreal

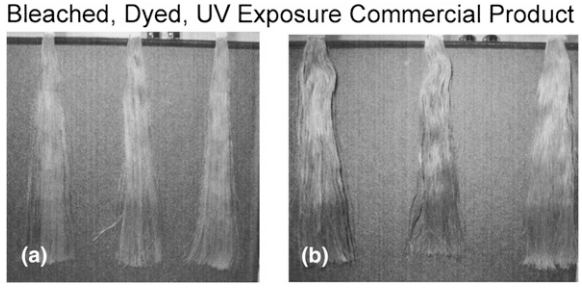

Figure 5. (a) Exposed area on hair tresses treated with commercial control: Very distinctive and perceptible color loss; (b) Exposed area on hair tresses treated with zinc oxide and jojoba oil: Very slightly perceptible color loss compared to commercial control.

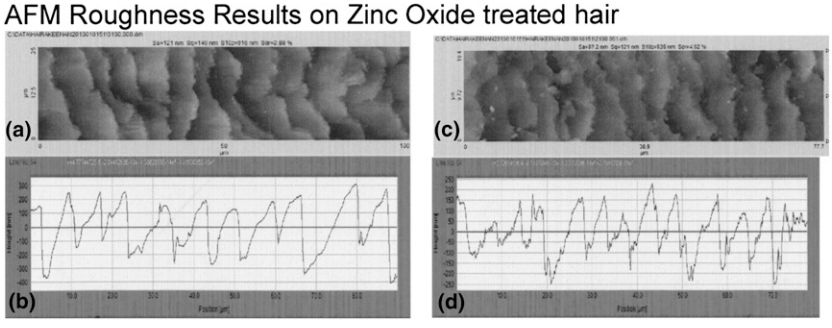

Figure 6. (a,b) Untreated control. (c,d) Tress treated with zinc oxide and jojoba oil.

such as the scales or small particles that may be the zinc oxide was found by one technique, it was typically seen by the other. Subtle changes in the topography of the hair may be seen by comparing the line profile before and after treatment of the hair with zinc oxide and jojoba oil (Figures 6b and 6d). The small differences in the profile are due to the addition of zinc oxide to the hair surface. These differences suggest a rather good distribution of the zinc oxide without gross clumping of the material and with a very small effect on the topography of the hair. In most cases, the treatment is not thick enough to obliterate or cover over the individual scales. The treatment does increase the roughness of the scales by deposition of the zinc oxide on a nano scale, but panelists feel the effect of the jojoba oil, and overall surface roughness is relatively unchanged. The addition of the zinc oxide then allows protection of the hair from UV damage and color loss protection by light-scattering mechanism. Distinctive domains of zinc oxide are evident in areas where the hairs touch or overlay on the hair fiber surface even after exposure to UV light. The hair, as tested by panelists after UV exposure, still maintains a natural, uncoated, and non-greasy feel.

During the UV exposure, the hair tresses were clamped so the middle was exposed, and the top and bottom were covered and not exposed to UV; the whole tress was exposed to 50°C temperature during the duration of the test.

The top and bottom protected portions of a single hair tress were compared to the middle exposed area for average surface roughness and peak to valley height. Surprisingly, the middle exposed cuticles did not appear uplifted or damaged after 168 hrs of continuous 313λ nm at 50°C. Indicating the middle area treated with zinc oxide not only offers color protection but additionally offers hair surface damage protection. See Figures 7a, b, and c.

The zinc oxide does not overshadow the treatment. By having a fine distribution of zinc oxide across the hair shafts, color loss protection and UV damage protection are obtained, without negatively impacting aesthetics. The hairs still feel and look natural as observed by expert panelist. The treatment benefits of the zinc oxide and jojoba oil were observed across Caucasian, Latin, and damaged bleached hair types; and would offer benefits across all hair types.

SEM ZINC MAPPING RESULTS FOR ZINC OXIDE AND JOJOBA OIL

SEM images show the morphology of the hair and the treatment distribution. In this series of images we used bleached, dyed hair tresses treated with zinc oxide and jojoba oil, then exposed to UV. Due to atomic number contrast, the zinc oxide material appears brighter than the hair. X-Ray mapping shows the zinc distribution for the zinc oxide materials. Phase maps, in which pixels with similar spectra are grouped together, show two phases (hair and background) for the control samples and three phases (hair, background, and zinc-rich) for the zinc oxide samples. Overlays of the zinc-rich phase maps

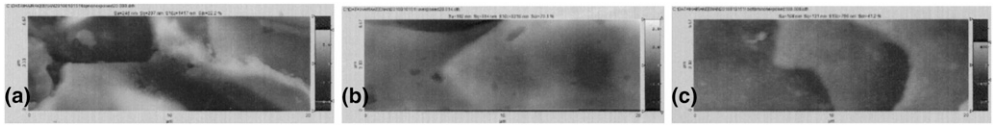

Figure 7. (a) Top covered. (b) Middle exposed. (c) Bottom covered.

onto the SEM images (Figure 8) show the location of the zinc-rich domains. There does not appear to be a dramatic difference based on hair type. After 168 hrs of UV exposure, (Figure 9), the zinc oxide morphology is unchanged and there is continuous UVA/UVB protection and prevention of color loss. This confirms the UV damage protection and color loss protection benefits of zinc oxide and jojoba oil across many hair types.

ANTI-FRIZZ AND HUMIDITY RESULTS FOR ZINC OXIDE AND JOJOBA OIL ON AFRICAN HAIR

To better simulate the conditioning and antifrizz benefits of zinc oxide and jojoba oil, African hair tresses treated with zinc oxide and jojoba oil were exposed to 90% RH and 30°C for 4 hrs. The zinc oxide/jojoba oil treated tress has reduced frizz and more control than the commercial control or untreated control (Figure 10; Table V).

Expert panelists evaluated hair tresses after treatment, and the results are show in Figure 11 below. The feel of the hair tresses is improved compared to the control cream without zinc oxide and jojoba oil. These tresses felt smooth and did not feel greasy. The addition of the zinc oxide to the surface of the hair did not negatively impact the other properties. The benefits of the jojoba oil would be for very curly or tightly curled hair that is not easily managed, such as Brazilian or African hair. It offers controlled frizz and a smooth conditioned feel.

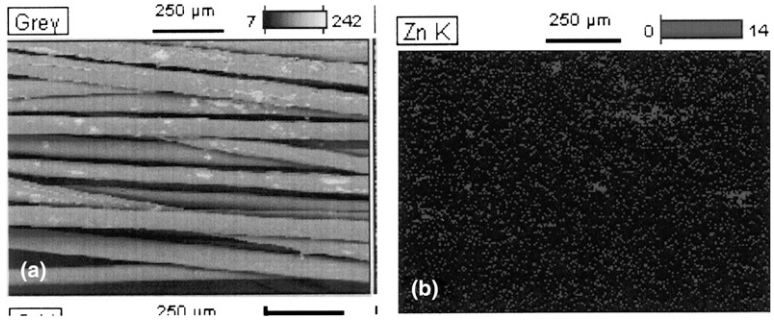

Figure 8. (a,b) Overlays of zinc-rich phase maps onto SEM images.

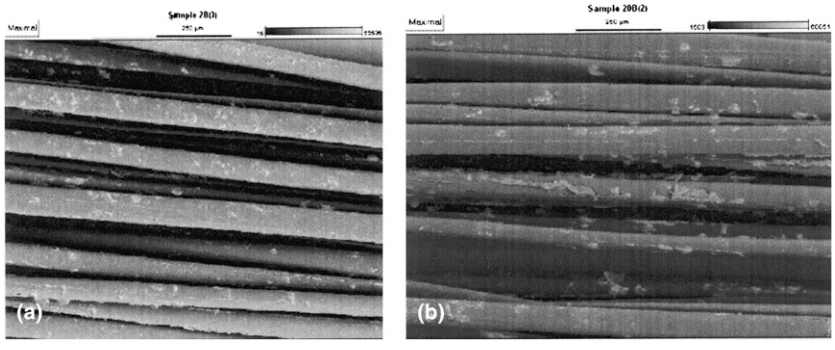

Figure 9. Overlay on UV-exposed (a) European bleached hair and (b) Brazilian curly hair.

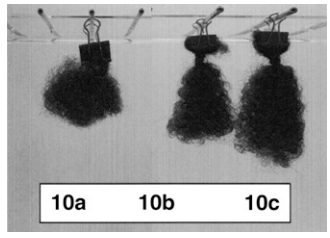

Figure 10. (a) Untreated. (b) Zinc oxide/jojoba oil-treated. (c) Commercial control

Table V
Anti-Frizz on African Hair after Exposure to 90% RH, 30°C for 4 hrs

10a Untreated hair	Very frizzy
10b Zinc oxide and jojoba oil-treated	Minimal frizz
10c Commercial control	Moderate frizz

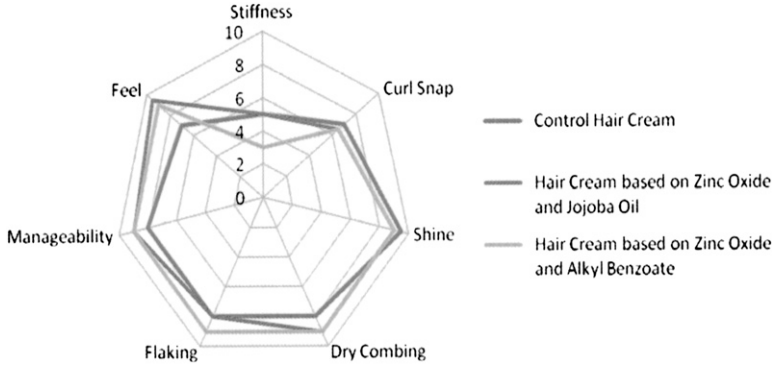

Figure 11. Hair panelist evaluation of Brazilian Latin hair, average of three tresses. Zinc oxide and jojoba oil cream on Latin hair; hair characteristics by panel evaluation.

POLYQUATERNIUM 10 AND 67 FOR ENHANCED FEEL AND CONDITIONING

Polyquaternium-10 and polyquaterniun-67 have functionality for conditioning benefits on hair through a shampoo but have additional benefits provided directly from a styling product for conditioning, combability and feel. They provide ease of comb (wet and dry), improved feel (softness/smoothness), and manageability. As demonstrated in Figure 12a,b where a split end is observed, after treatment with polyquaternium 10 there is repair of the split providing improved conditioned feel and smoothness, and hair repair.

The polyquaternium-67 and acrylates/hydroxyesters acrylates copolymers were incorporated into a curl activator spray and shown to provide curl definition and anti-frizz on Brazilian curly hair and Asian hair. In addition, the acrylates/hydroxyesters acrylates copolymer is a film former and aids in improved high-humidity curl retention. Polyquaternium-10 and 67 are strongly conditioning, providing efficient frizz control and curl definition; they can be recommended for normal to "difficult" hair types (frizzy, curly) and from Asian hair to Brazilian curly hair (see Figure 13; Table VI).

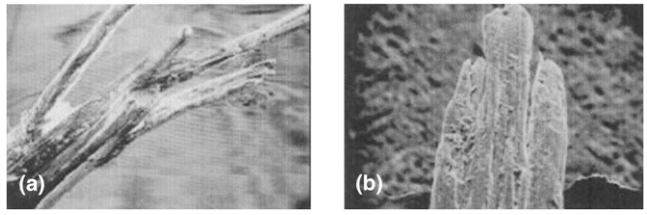

Figure 12. (a) Hair fiber—split end. (b) After treatment with PQ10.

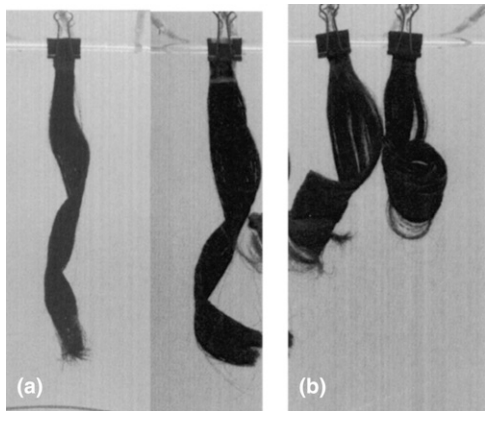

Figure 13. (a) Untreated Asian and Brazilian hair. (b) Treated Asian and Brazilian hair.

Table VI
% Curl Retention after Exposure to 90% RH and 30°C

	Initial	4 hr	8 hr
13a1 Untreated Asian hair	100	40	10
13a2 Untreated Brazilian hair	100	50	20
13b1 Treated Asian hair	100	70	50
13b2 Treated Brazilian hair	100	80	55

CONCLUSIONS

a. To address the needs of the diverse ethnic market a variety of hair care products is required to meet the various demands. For shine, style control and humidity resistance and non-flaking: a formulation based on acrylates/hydroxyesters acrylates copolymer will provide these attributes. This is shown on hair tresses using standard personal care methods and substantiated using AFM techniques. These film forming polymers have utility across a variety of hair types, including European, Brazilian, African, and Asian. There was significant improvement in shine and hold for Caucasian hair, as well as Brazilian and African.

b. For color protection and UV damage protection, incorporating zinc oxide and jojoba oil into a treatment will provide these benefits. In addition there will be enhanced frizz control and a conditioned feel. This was verified using treated UV exposed tresses and corroborated using SEM techniques to monitor the zinc distribution and AFM techniques

for cuticle damages. The Zn does not overshadow the treatment. By having a fine distribution of zinc oxide across the hair shafts, color protection and damage protection are obtained, without negatively impacting aesthetics. The hairs still feel and look natural as observed by expert panelists. The type of protection and conditioning attributes can be specifically targeted to curly hair, such as Brazilian and African as well as any color-treated hair.

c. By using polyquaternium-10 or 67 into a hair care treatment, there are improvements to the feel, smoothness and antifrizz repair. Using SEM and AFM there is indications of hair repair after treatments. This is critical for tightly curled hair types, including African and Brazilian.

d. Overall, many of the needs for this diverse and growing market segment can be met by utilizing a combination of products, with targeted benefits depending on the hair type.

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