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Approaches to polymer selection for mascara formulation

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Synopsis

The use of hair-care and hair-styling polymers in mascara formulation is well known. This paper introduces pre-formulative evaluation of film formers which are intended to be applied on eyelashes for mascara development to screen film formers more effectively. The film-forming characteristics of randomly selected hair-styling polymers were evaluated under the influence of pH, temperature, surfactant, and pigment dispersion. The selected polymers included acrylics, polyurethanes, and a pyrrolidone, all of which are used throughout the hair-care and mascara industries. An Erichsen Model 299/300 Pendulum Damping Tester was used to determine film hardness. In analyzing samples by the effect of temperature, the hardest neat polymer, a styrene-acrylate, softened 30% after heating. For most of the other polymers, the hardness was slightly lower compared to the neat polymer. The addition of pigment didn't significantly influence the hardness of one acrylic copolymer and a urethane dispersion, but most of the other polymers exhibited a reduction in film hardness. Various hardnesses were observed with different surfactants and different pH's.

INTRODUCTION

The key to successful mascara formulation is a flexible lash-styling and shape-holding coating. The complex physical-chemical structure of mascara comes from the relationship between waxes, film formers and other functional ingredients. The polymer behavior after interaction with other constituents in mascara formulation unpredictably changes. The empirical way of polymer selection requires a number of mascara batches until the right polymer will be chosen for the particular mascara system.

Traditionally, the selection and testing of polymers for mascara formulations is based on related hair-care and hair-styling technologies, but mascara technology is different than a hydroalcoholic solution of film-forming polymers, aerosol foams and setting hair gels which are used in the majority of hair-styling products.

Although hair-spray technology seems to be not that close to mascara formulation, it could be considered in terms of film formers and testing of their properties.

The essential components of hair styles and hair sprays compared to mascara are presented in Table I.

Reviewing formulations for hair products in comparison to mascara (Table II) shows that mascara development requires special thought for selection of film-forming polymers.

Table II represents the similarities and differences in formulation approaches for these products.

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Table I
Comparison of Essential Components of Hair Sprays/Styles and Mascara

Essential components of hair sprays	Essential components of hair styles	Essential components of conventional mascara
Film-forming polymers	Film forming polymers	Film-forming polymers
Plasticizers for polymers	Plasticizers for polymers	Plasticizers for polymers
Glossing agents	Disentangling, softening, and glossing agents	Waxes
Solvents	Solvents	Pigments
Propellant	Perfume	Surfactants
Perfume	Colorants	

Table II
Comparison of Formulation Approaches of Hair Sprays/Styles and Mascara

Formulation approaches for hair sprays	Formulation approaches for hair styles	Formulation approaches for conventional mascara
Good spraying results in very fine droplets	Improvement of hair style hold	Flexible coating of lashes
Formation of transparent or clear, translucent film	Easy application on wet hair	All-day lash hold
Flexible, elastic film without breaking with hair movement	Easy combing	No-flake wear
Adequate substantivity of film to hair keratin	Does not feel sticky	Easy gliding
Enhanced gloss	Quick drying time	Quick drying time
Rapid drying	Does not become powdery when brushed or combed	Increased lash fullness
Absence of a sticky, tacky feel	Ensures hair body and bounce	No-clump application
Non-hydroscopic	Increased hair volume	Supple lashes
Easy to brush out	Hairs do not clump	Non-hydroscopic film
Easy to remove with shampoo	Non-hydroscopic film	Non-sticky or tacky film
	Greater hair gloss	Easy to remove with makeup remover or soap and water
	Does not cause excess stiffness	

As seen in Table II methodological differences in formulation approaches of hair products and mascara are significant. A better understanding of polymer selection for mascara by functional properties requires the development of specific methods for polymer evaluation for mascara application. Among other factors, the film hardness is an important characteristic of film forming polymers.

This paper is an attempt to adopt a test for film hardness of paint and related coatings to the selection of polymers for mascara application during the pre-formulation stage. The practical advantages of these experiments might be helpful for screening film formers for mascara, cutting time during the empirical stage of product development.

MATERIALS

This study was conducted on randomly selected film formers, as listed in Table III. Film-forming characteristics were evaluated under the influence of the following factors: pH,

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temperature, surfactants, and pigment dispersion. These factors are typical for mascara compounding.

METHODS

EVALUTION OF FILM HARDNESS

An Erichsen Model 299/300 Pendulum Damping Tester was used to determine the film hardness (Figure 1).

Samples were drawn down on 7×4×1/8 inch untreated glass plates. A Byk-Gardner 6-mil wet film drawdown bar was used to draw down all samples.

The bar was pulled down at a steady rate and was pulled off the glass plate to leave a 3-mil coating. This was set aside to dry at room temperature for 24 h. Hardness measurements were then taken three times and averaged.

Table III
Study Materials

Sample	Chemistry of film former	Heat tolerance	pH Range	% Solids
A	Styrene acrylates copolymer (microemulsion)	Up to 50°C	7–8	25
B	Acrylates copolymer (Solution)	Up to 50°C	7–8	25
C	Polyurethane (microemulsion)	Up to 50°C	7–8	33
D	Styrene acrylates copolymer (dispersion)	Up to 50°C	7–8	40
E	Acrylates copolymer (dispersion)	Up to 50°C	7–8	40
F	Polyurethane* (dispersion)	Up to 50°C	8–9	40
G	VP/VA in water and propylene glycol* (solution)	Up to 50°C	5–6	48

*The pH factor was evaluated when the pH was adjusted to neutral (pH 7–8).

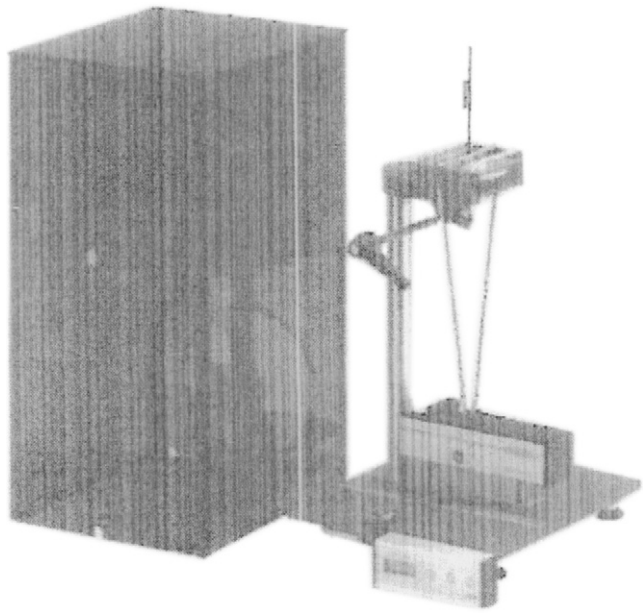

Figure 1. Pendulum damping tester Model 299/300.

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The principle of the pendulum film hardness test is based on the fact that the amplitude of oscillations of a pendulum rocking on a sample decreases more rapidly the softer the film. The tester was set up to measure the number of oscillations.

The factor-properties relationship regarding film formation was tested with regard to the following factors: pH, temperature, presence of surfactant, and pigment dispersion since these are common factors involved in mascara manufacture.

To determine the effect of temperature, Samples A, B, C, D, E and G were heated to 50°C cooled to 25°C, then drawn down as described above. Sample F was heated to 40°C, cooled to 25°C, then drawn down.

To determine the effect of surfactant, the samples were heated as described above and mixed with 0.5% of surfactant. Two surfactants were employed: one with an HLB of 17, the other with an HLB of 4. The samples were cooled to 25°C and drawn down.

To determine the effect of pigment, 5% of black iron oxide was added to the film former and mixed under high shear at 2000 rpm for 15 minutes at room temperature, then drawn down.

To determine the effect of pH, Samples F and G were adjusted to between pH 7 and 8 with isostearic acid and triethanolamine, respectively.

EVALUTION OF POLYMERS FOR MASCARA APPLICATION

A conventional mascara (O/W system) was prepared using the same amount of each polymer. A total of 7 mascara samples were prepared. The samples were filled in the same pack with the same applicator and applied to human lashes in a consistent manner with 30 strokes. Digital images of the eyelashes were taken and analyzed. The final judgment on product performance included lash image analysis and panelists' perception of product attributes.

RESULTS AND DISCUSSION

The changes in film hardness are presented in Figure 2–8. In terms of the film hardness of the neat polymer, Sample A (Figure 2) was the hardest and Sample E (Figure 6) was the softest, but that changed with the different factors. Regarding the effect of temperature, for almost all heated polymers, the hardness was lower than that of the neat polymer. Only Sample G exhibited an increase in film hardness, which seemed brought about by the temperature.

Overall, the film-forming properties of Sample E (Figure 6) were in line with the film hardness of the untreated polymer. Samples C and D showed modification of film hardness compared to the untreated state (Figure 4 and 5).

The addition of pigment didn't significantly influence the hardness of Samples E and F, while Sample A, B, C, and D exhibited a reduction in film hardness. Interesting functional properties were observed with Sample G (Figure 8), however. As mentioned above the film hardness of this polymer significantly increased under the influence of temperature. The same trend was observed under the influence of surfactants and pigment. The hardness of the film declined at least by half when the pH was adjusted to neutral (Figure 10).

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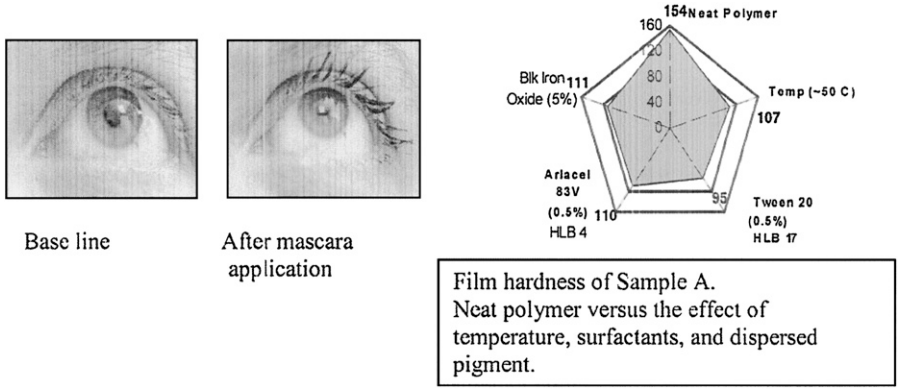

Figure 2. Sample A (styrene acrylates copolymer, microemulsion).

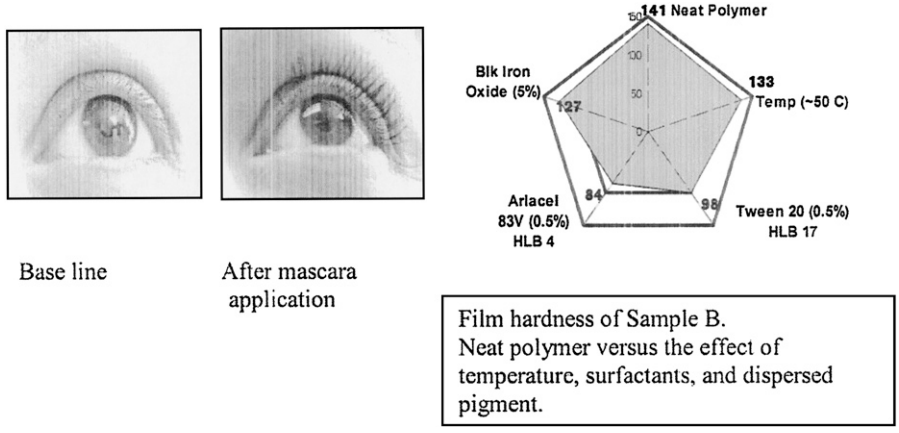

Figure 3. Sample B (acrylates copolymer, solution).

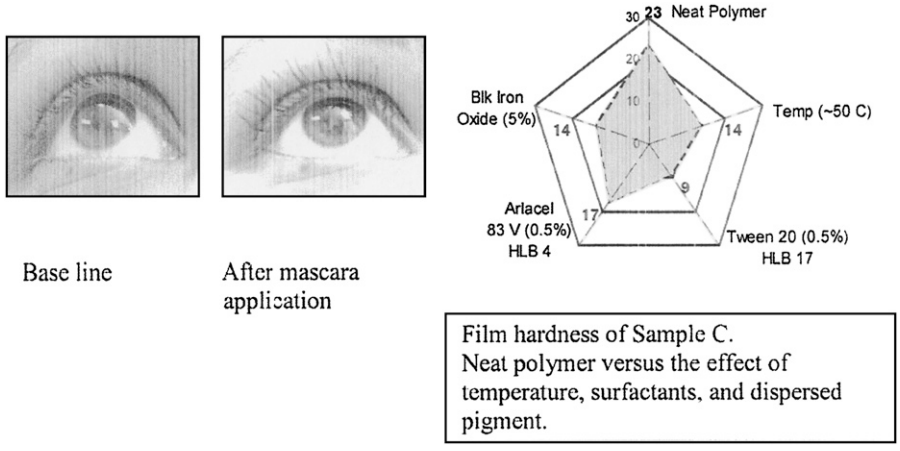

Figure 4. Sample C (polyurethane, microemulsion).

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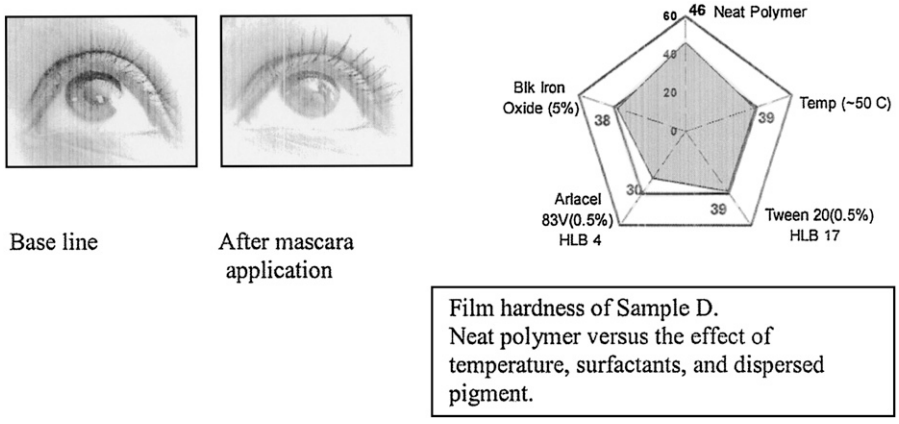
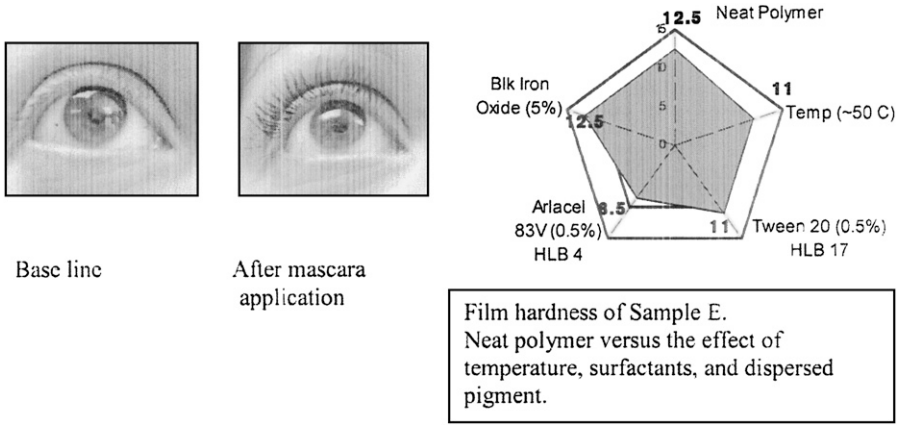


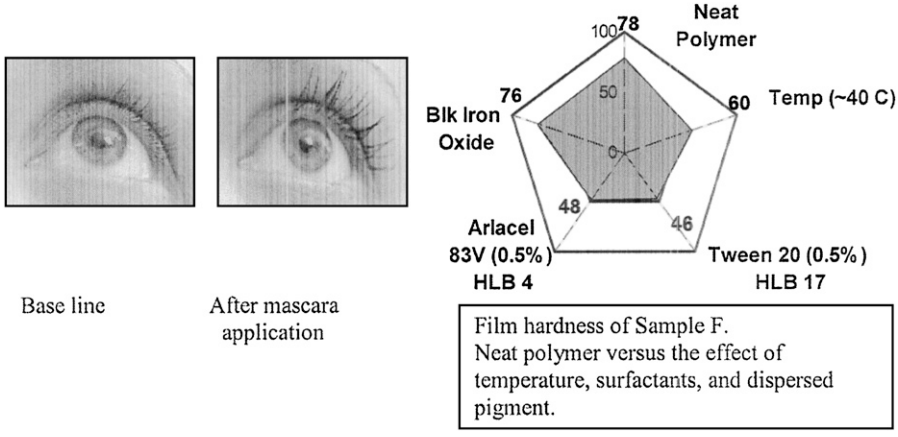
Film hardness of Sample D.
Neat polymer versus the effect of temperature, surfactants, and dispersed pigment.

Figure 5. Sample D (styrene acrylates copolymer, dispersion).



Film hardness of Sample E.
Neat polymer versus the effect of temperature, surfactants, and dispersed pigment.

Figure 6. Sample E (acrylates copolymer, dispersion).



Film hardness of Sample F.
Neat polymer versus the effect of temperature, surfactants, and dispersed pigment.

Figure 7. Sample F (polyurethane, dispersion).

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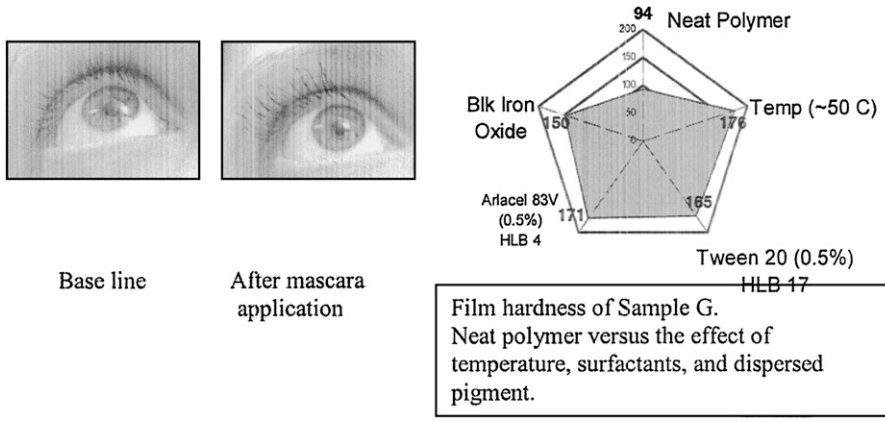

Figure 8. Sample G (VP/VA in water and propylene glycol, solution).

Figures 9 and 10 show the difference in film hardness between film formers with their original and adjusted-to-neutral pH's. Both samples exhibited a decrease in film hardness when their pH's were adjusted to between 7 and 8, a common pH range for liquid eye cosmetics.

Taking into consideration the evaluation of mascara performance versus the selected polymers shows that it is not the actual film hardness that changes, but that all of the polymer properties are influenced by the different factors in a typical mascara system.

In understanding polymer selection for mascara development it is important to consider that this selection is conducted for each particular formula and brush combination and the results can vary widely with different applicators.

Samples A, C and F showed a softer film with the experiments with Tween 20. Using those polymers in our formula showed a good lengthening effect on lash images but unsatisfactory lash separation (Figures 2, 4 and 7), as would be expected with our O/W mascara formula with Tween 20.

Samples B, D and E exhibited similar changes under the influence of the experimental factors resulting in similar mascara performance (Figures 3, 5 and 6). These polymers provided an acceptable volumizing effect and comparable separation with the tested formula/brush combination. Sample G was an exception because of the increase in film hardness under all the experimental factors compared to the neat polymers. A significant increase in film hardness based on the percentages used in our system resulted in the product sticking to the brush bristles and a decrease in product delivery to the lashes (Figure 8). The next possible step for a formula adjustment with this polymer would be decreasing its amount in the formula or plasticizing the film former for better performance with the tested formula/brush combination.

SUMMARY OF OBSERVATIONS

1. The practical advantages of these experiments might be helpful for screeing film formers for mascara development, especially for tight time projects.
2. This method gives formulators the opportunity to anticipate the behavior of film formers under different factors such as pH, temperature, surfactant, and pigment

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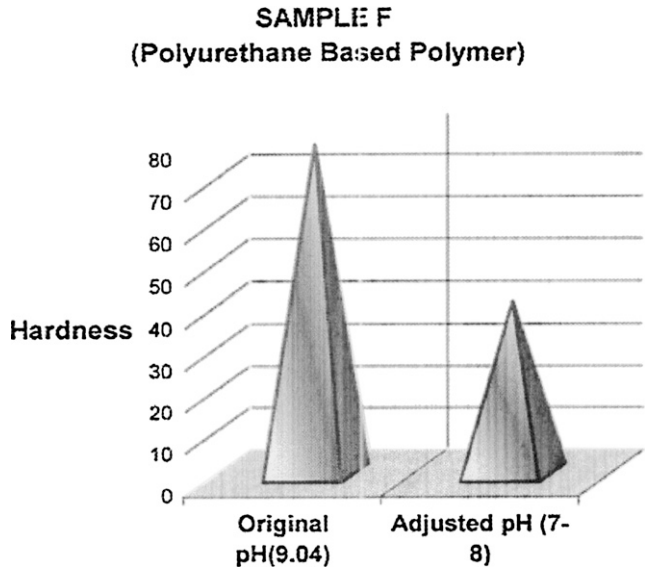

Figure 9. The effect of pH on film hardness.

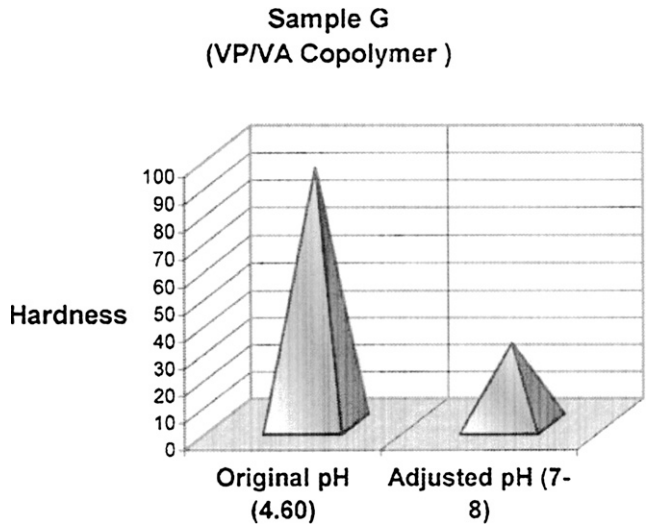

Figure 10. The effect of pH on film hardness.

dispersion during pre-formulation, and enables them to select softer or harder polymers—or a blend of both—for a balanced system.

3. Our experiments showed a modification of film hardness under the several factors such as pigment interaction, adjusting the pH of the polymer, adding surfactant (high or low HLB), and the effect of temperature.
4. The experiments allowed us to differentiate a suitable emulsion system to achieve the desired properties of the polymer.

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5. The neat polymer may not exhibit the hardness desired, but may be more appealing when subjected to heat or blended with typical formulation ingredients (surfactants, pigment), as can be seen with Sample G.
6. More data need to be compiled on polymers with similar technology in order to better understand the correlation between film hardness and the performance of the final product, especially the effect of different pH adjusters on film hardness as well as the effect of various emulsifiers.
7. The hardness test does not necessarily correlate with mascara performance, but it helps to define the formulation approaches and better understanding of polymer performance in a mascara formula.

All of these factors, and their effect on the final formulation, continue to be investigated in our laboratory.

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