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Novel multifunctional film-forming system

Film-formers are used extensively in personal care formulations. In hair care applications they can be used to aid styling and enhance shine; in skin care and sun care they can protect the skin, add water-resistance and ensure the even distribution and adherence of active ingredients. Film-formers are particularly important in colour cosmetics where they can increase the wear properties of formulations such as lipsticks, mascaras, eyeliners, eyeshadows and foundations. They can have a significant effect on the ease of application of a cosmetic product as well as the appearance of the product on the skin, and the length of the time that the product remains on the skin.
A wide range of both oil-soluble and water-soluble film-formers are currently used, all with their own advantages and disadvantages. Formulators and consumers look for different properties in film-formers at different times. In general the most desirable film-formers would create films that are:

- Strong and long-lasting
- Quick drying
- Non-tacky
- Light and comfortable on the skin
- Easy to remove when required
- Able to hold and deliver active ingredients
- Cost-effective

Alzo International has developed a new film-forming system for personal care applications which provides all of these desirable benefits in a system that is easy to use and compatible with many different types of formulation. Alzo has named this system NuPLastic, and it consists of a Polyderm polyurethane dispersion and a NuLastic silicone elastomer,[1] which work together to give long-lasting, flexible, emollient and versatile films. The film forms as the formulation sets onto the skin, and the NuPLastic system can be tailored to be extremely fast drying, often taking less than a minute from wet application to formation of a dry film, even when containing a high percentage of oil phase. What makes this system unique is that the NuLastic silicone elastomer acts as a plasticiser for the Polyderm polyurethane dispersion,[2] enabling the cosmetic formulator to benefit from the strong films formed by the polymers, but with a vastly improved skin feel and ease of formulation.

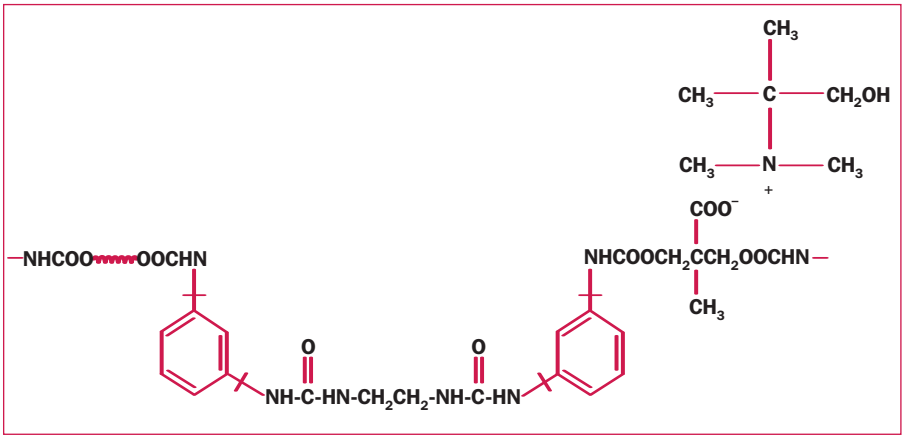

Figure 1: *The structure of the Polyderm PE-PA ED Thermoplastic Polyurethane Elastomer.*

The NuPLastic System (hereafter referred to as 'the new film-forming system') consists of two Alzo International polymer technologies:

Thermoplastic Polyurethane Elastomer resin as the film-former

Polyderm PE-PA ED (INCI name: Polyurethane 58) is a water based polyurethane polyether microemulsion resin (polyether-propionic acid/TMXDI copolymer) made by the reaction of a polyether diol containing two hydroxyl groups and an acid with a diisocyanate. Figure 1 shows the structure of this polyurethane molecule. Polyderm PE-PA ED Thermoplastic Polyurethane Elastomer (TPE) is hereafter referred to as 'the TPE'.

Table 1: Description of NuLastic thermoset silicone elastomers.

NuLastic Type	INCI name	Chemistry	Available cross-linked in these media
NuLastic Silk-E	Polysilicone 23	Silicone elastomer with ethoxylated and cationic chains which allow some emulsification	• Isododecane • Dimethicone • Isononyl Isononanoate
NuLastic Silk	C_{4-24} Alkyl Dimethicone/ Divinyldimethicone Crosspolymer	Silicone elastomer with 4–24 alkyl chains	• Cyclomethicone • Isododecane • Dimethicone • Isononyl Isononanoate
NuLastic Surfa	Bis-Vinyldimethicone/PEG-10 Dimethicone Crosspolymer	Silicone elastomer with hydrophilic, ethoxylated chains which allow emulsification	• Isododecane • Dimethicone • Isononyl Isononanoate

Figure 2: *Polyderm PE-PA ED Thermoplastic Polyurethane Elastomer dispersed in water; as the water evaporates the concentration of the TPE increases to above 33%, at which point the TPE film is formed.*

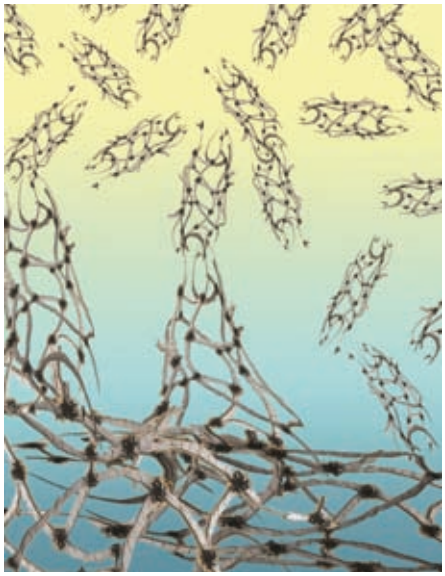

Figure 3: *NuLastic Thermoset Silicone Elastomer dispersed in solvent; as the solvent dissipates the concentration of the TSE increases to above 10%, at which point the TSE film is formed.*

Figure 4: *The combination of the Polyderm PE-PA ED Thermoplastic Polyurethane Elastomer and the NuLastic Thermoset Silicone Elastomer results in a hybrid NuPLastic film that is strong, flexible, quick-drying and non-tacky.*

Thermoset Silicone Elastomer as the plasticiser

Different NuLastic Thermoset Silicone Elastomers (TSEs) can be used in this system to achieve different effects, and several options are described in Table 1. In all cases, the cross-linked silicone elastomers have a three-dimensional cage-like structure which gives them the ability to gel solvents. Compatible solvents include volatile compounds such as cyclopentasiloxane and isododecane, and non-volatile compounds such as cosmetic esters and oils. These solvents occupy the spaces formed by the cross-linked structure and cause the structure to swell. The NuLastic Thermoset Silicone Elastomer is hereafter referred to as 'the TSE'.

Thermoplastic Polyurethane Elastomers

Polyurethanes are polymers consisting of chains of organic units joined by urethane links (RO(CO)NHR). The key benefits of the TPE used in the new film-forming system are that it dries to a clear and cohesive film, has good adhesion to skin and hair, and is both chemically-resistant and water-resistant. Water-based TPE dispersions also have inherent surfactant behaviour and so create self-emulsifying systems, reducing the need for external emulsifiers. In this form, the TPE molecules are not cross-linked.

Thermoset Silicone Elastomers

TSEs are often used in cosmetic formulations, usually to provide a silky, smooth and emollient skin feel. They are composed of polysiloxanes (polymers with a silicone backbone), which are then cross-linked to form a 3-dimensional structure that gives elastomeric behaviour. These cross-linked elastomers are thermoset materials which cannot be reheated and melted to be shaped differently. The polysiloxane properties can vary greatly, depending on the molecular weight, whether the structure is linear, branched or cross-linked, and the nature of the terminations of the polymers.

When TSEs are diluted or dispersed in a solvent or liquid, the solutions give a very smooth, non-oily, dry feeling on skin and hair, which is generally well-liked by consumers. This smooth feel is particularly useful in colour cosmetics that contain pigments, because it improves the application of the product.

When using an elastomer with a non-volatile carrier, such as isononyl isononanoate, the ester is entrapped within the voids of the polymer, allowing for the loading of up to 50% of a lipophilic material. This results in an outstanding emollient film that is highly desirable when applied to the lip or skin. In addition these entrapped oils add shine, sheen and lubricity. The entrapped ester exudes from the cross-linked network over time, allowing the extended and prolonged delivery of the emollient which further adds to the system's sensory appeal. It is also possible to entrap fragrances and other olfactory compounds. The cohesion of the silicone elastomer helps to hold the film and any entrapped ingredients on the skin or hair.

In addition to these benefits, Alzo International has discovered that TSEs can act as plasticisers for water-based or water-dispersed thermoplastics.

Plasticisers are defined by the American Society for Testing and Materials (ASTM) as substances incorporated into a plastic to increase flexibility, workability and distendability.[3] Plasticisers improve the performance and versatility of many plastics in this way, in many applications. Plasticisers act as a 'spacer' between molecules, increasing the distance between molecules and decreasing the cohesive intermolecular bond, making the plastic softer and more flexible. The most effective plasticisers are those that are not reacted with the thermoplastic polymer but interact physically with it.

In addition to softening the plastic polymer, plasticisers also lower the temperature at which the plastic can be processed, reduce the stickiness of the plastic during processing, and improve the surface appearance of the plastic. Colour cosmetic formulations such as lipsticks usually use an ingredient such as an ester or oil as a plasticiser, as they soften the waxes in the formulation and improve the adhesion of the formulation to the lip. Resins used in hairsprays and nail polishes have traditionally used solvents such as esters and oils to make the polymers more flexible, easier to apply and with improved adhesion to the hair or nail.

Synergistic effect of the new film-forming system

In the new film-forming system, the TSE and the TPE are combined and work synergistically to give a novel film-forming material. The degree of rigidity of the film formed by the TPE film-former depends on the degree of intermolecular bonding

between the polymer chains. The TSE plasticiser decreases the rigidity of the TPE film by lubricating at a molecular level. Also, as the TPE chains come into contact with each other, there will be free spaces between the polymer chains, and the TSE plasticiser can occupy these spaces. This increases the intermolecular spacing between the polymer chains of the TPE, and so decreases the strength of the intermolecular bonds. This decreases the rigidity of the TPE film, making it softer and more flexible, with better adhesion to the skin.

The TSE also modifies the feel and behaviour of the TPE film. The other benefits of these cross-linked gels are that they provide a lubricious and emollient skin feel, the ability to suspend solid particles, viscosity modification, and the possibility to deliver both oil-soluble and water-soluble ingredients.

Figures 2 to 4 show the TPE alone, the TSE alone, and the combination of the two when used in the new film-forming system. These diagrams illustrate the ability of the TSE to act as a spacer between the TPE chains, plasticising the resultant film.

Most water-dispersible thermoplastic resins, such as Alzo's TPEs, tend to be low in viscosity, allowing them to diffuse into the substrate, in turn leading to better adhesion and better film attributes. The use of a TSE as a plasticiser and emulsifier increases the viscosity of water-dispersible thermoplastic resins, allowing solid particles such as pigments, pearls, and solid active ingredients to be used at high levels without sedimenting. The viscosity of the emulsion can be varied to the required level by varying the level of silicone elastomer – the higher the level of silicone elastomer, the greater the viscosity of the emulsion. This variability is another great benefit of using the new film-forming system in pigmented makeup and lip products.

The Alzo TSEs which are gelled by volatile solvents set in a matter of seconds. This can help to create fast-drying films in formulations: films formed by the new film-forming system can set in less than a minute, unlike other film-formers which may take 5 to 10 minutes to dry. This is obviously a highly beneficial feature of combining TSEs with TPEs. Another benefit is the ability to develop transfer resistant products, which are typically associated with colourants such as pigments, dyes and pearls in mascaras, lip products, eye shadows, blushes and foundations. In these respects, the use of these silicone elastomers as plasticisers contributes to 'long wear', in which the film maintains its integrity on the surface to which it has been applied.

Figure 5 shows the difference in transfer-resistance between a conventional lip gloss and one made with the new film-forming system. These photographs show that using the new film-forming system in a lipgloss formulation reduced the amount of lipgloss that could be transferred onto a white tile.

As we have discussed, the new film-forming system combines the film-forming benefits of the TPE with the skin-feel and oil/ester-entrapment benefits of the TSE. The combination of both materials also adds several other advantages to the formulation, including:

- Forms a fast-drying film – less than a minute from wet application to dry film
- Eliminates tack
- Increases the flexibility and permeability of the film
- Increases transfer-resistance and water-resistance of the TPE
- Acts as a sponge to entrap non-volatile solvents in the film
- Film can deliver both oil- and water-soluble actives
- Film can entrap fragrances

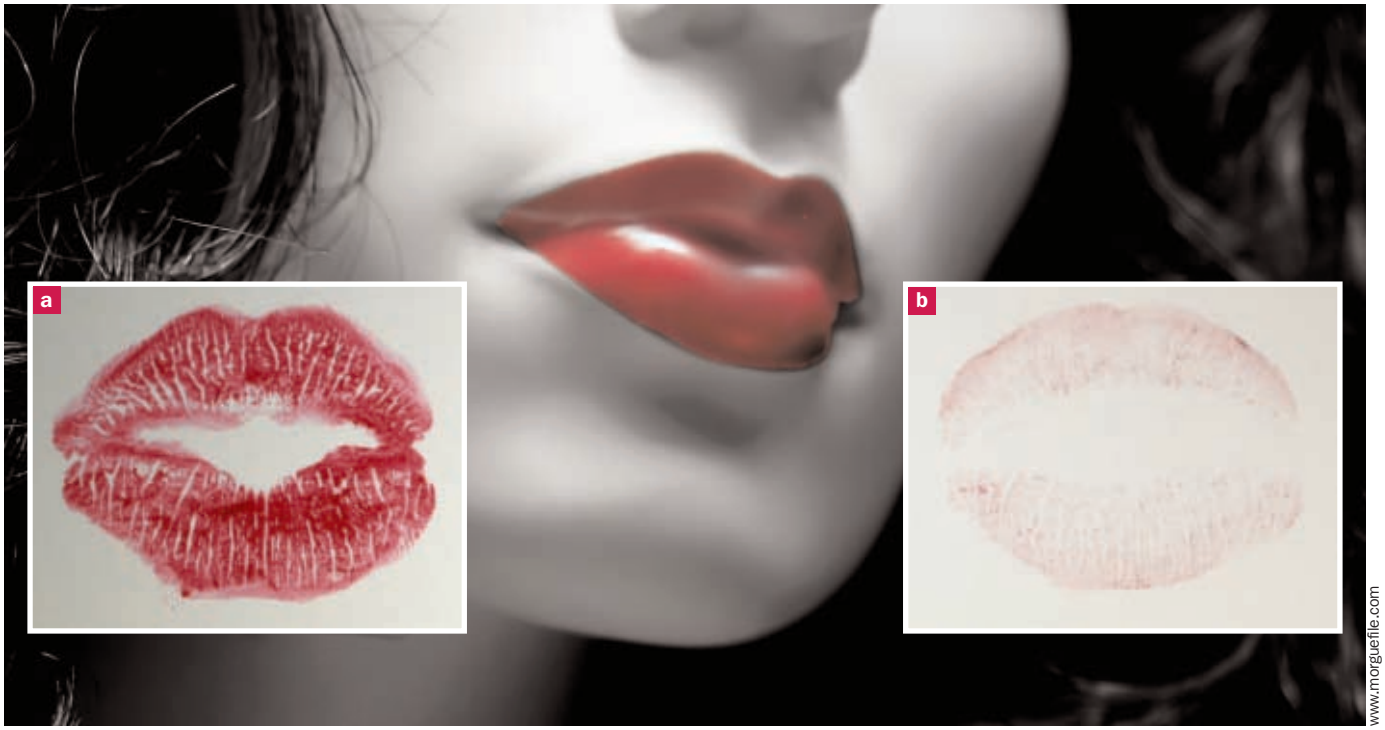

Figure 5: a) *Conventional lipgloss transference onto a white tile.* **b)** *NuPLastic System lipgloss transference onto a white tile, clearly showing that significantly less gloss is transferred from the formulation using the NuPLastic film-forming system.*

Formulating with the new film-forming system

Alzo's TSEs work best with non-polar oils, esters, and other solvents such as dimethicone, isododecane, cyclomethicone and isohexadecane. The TSE gel will increase in viscosity as the percentage of solids such as pearls, oxides, fumed silica and other fillers are increased, creating emulsions with a 'mousse'-type texture.

The TPE acts as the film-former and also as an emulsifier. The studied TPE is the preferred TPE to use in this system as it uses two aminopropanols to disperse 33% polyurethane in water. As aminopropanols are anionic this creates an ionic emulsion. Above pH 8 the TPE is in solution with the smallest possible particle size. As the pH decreases below 8, the particle size of the TPE increases, to form the film and introduce water-resistance. This drop in pH can be achieved by adding low pH ingredients to the mixture, or by the evaporation of the volatile aminopropanols. After the aminopropanols have evaporated, the film no longer contains emulsifiers, which gives it its water resistance. Adding non-volatile emulsifiers to the system can lead to longer drying times for the film, and result in films that are tackier.

The TPE film-former needs to be used at levels above 20%, and preferably at around 30%. The most robust films are required for lip products, and so higher percentages of the TPE would be recommended for this type of formulation. Products such as mascara and eye shadows do not need such robust films, and so lower levels of the TPE can be used.

The TSE changes the film created by the TPE resin into a hybrid film. Alzo's TSEs can exert this film-modifying effect even at very low polymer levels, such as 1% to 5%. The new film-forming system eliminates all tack usually associated with water-based film-formers.

Cationic ingredients such as bentones are compatible with the new film-forming system, but some cationic ingredients such as primary and secondary amines can cause instability. Hydrophilic ingredients can also cause instability and alter the properties of the film. High levels of solids can cause the film to become rubbery, which may be desirable in some applications and undesirable in others. Thicker films can create a long wear volumising effect. The new film-forming system can be used to create a 'topcoat' to seal undercoats of formulations such as lip products under a flexible, breathable film.

It is very quick and easy to make films using the new film-forming system, and a cold process can be used unless the formulation contains waxes that need to be melted. The formulation steps are:

- Mix 50% TSE using a mixer or homogeniser
- Add oil phase
- Add 30% TPE
- Add actives, pigments etc.

Conclusion

NuPLastic films have been shown to be transfer- and water-resistant thanks to the use of a silicone elastomer which acts as a plasticiser to the Polyderm PE-PA ED polyurethane film-former. This patent pending system is not product specific, so it allows users to customise specific film blends based on the selection of the specific silicone elastomer and polyurethane film-former. It is possible to vary the solvent (volatile or non-volatile) and to use the Polyderm PE-PA ED polyurethane with a silicone elastomer that either has emulsification properties (NuLastic Silk-E or NuLastic Surfa) or does not (NuLastic Silk), which will result in films with specific features and benefits for use in personal care products.

The result of this combination of materials is a truly unique and multifunctional hybrid film that can be used in many personal care formulations, providing the consumer with desirable features and benefits such as quick-drying, long-lasting, cost-effective, transfer- and water-resistant products that feel smooth and can deliver a wide range of active ingredients. PC

References

1 Patent: US6936686 B2. Cross-linked silicone gels: products containing the same; and methods of manufacture thereof. Publication date 30 August 2005.

2 Mosquera M, Mateu J. Silicone elastomers as novel plasticisers. *Speciality Chemicals* 2013; **13** (3): 18-19.

3 ASTM D883, Plastics Nomenclature.