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Formulating Low VOC Aerosol Hairsprays

Author: Dr. Matthias Pfaffernoschke

INTRODUCTION

Hairsprays in former times were formulated with chlorofluorocarbons (CFC) as propellants, which were abandoned after Rowland and Molina discovered in the mid-seventies that these chemicals cause a depletion of the ozone layer in the stratosphere. The ozone in the stratosphere is essential for protecting us, by absorbing UV radiation and not letting it pass through to the surface of the earth. Volatile organic compounds (VOC), which in hairsprays are for example, ethanol, hydrocarbon and dimethylether (DME) propellants, in combination with other gases such as nitrogen oxides (NO_x) emitted by cars and other sources, are considered to contribute to the formation of ground level ozone (“smog”), which harms the respiratory system.

Because of these environmental concerns, a great deal of research has taken place to develop polymers offering better compatibility and performance in water in order to formulate sprays with lower VOC levels. The driving force in the United States is the California Air Resource Board (CARB), which has implemented the maximum allowable amount of VOC in hairsprays to 80% as of January 1993 and to 55% as of June 1999. While this is only valid for the state of California, other US states followed in early 2005 and limited VOC use in hairsprays to 55%. In addition, under the current US legislation, some solvents and propellants (e.g. acetone, 1,1-difluoroethane (Hydrofluorocarbon 152a or HFC 152A)) are not considered to be VOCs because they show a low ozone creation potential and do not significantly contribute to the creation of ground level ozone.

While the legislation in the US is quite well defined, the member states of the European Union are still discussing whether a VOC restriction should be imposed on cosmetic products and at what level. However, some differences between the European Union and the US can already be seen. For example, the propellant HFC-152a is not considered a VOC in the US, but hydrofluorocarbons will not be an option

in Europe because of their rather high global warming potential (GWP), which contributes to the greenhouse effect. There are some countries in Europe that have implemented national laws to restrict the use of HFC-152a or have imposed taxes on VOC emitting products.

Extensive research continues to reduce VOC in hairsprays in order to meet the legislative requirements while maintaining the high level of product quality and performance expected by consumers. One of the options to achieve a low VOC content is to increase the water content of the hairspray formula; however, this can lead to various problems, such as an increase in solution viscosity, which translates to bad sprayability and foaming at the spray actuator and on the hair. Traditional polymers that were developed for alcohol-containing systems may not tolerate high levels of water, leading to possible resin instabilities. Also, the hold and the stiffness are affected if ethanol is simply replaced with water. Hairspray formulas that contain water have higher formulation viscosity and surface tension, which do not allow proper flow of the spray droplets down the hair, thus preventing the polymer from forming effective bonds between the hair fibers. Finally, corrosion of tin plated steel cans may become a problem due to the higher ion activity found in water-based systems. Therefore, new formulation strategies have to be adopted that include the use of surfactants and silicone-based glycol block copolymers such as Silsoft[®] 900 (INCI: PPG-12 Dimethicone; e.g. patent US 5853700 by Gormley et al.) to lower the surface tension of the spray in order to improve the spreading of the polymer droplet on the hair and the overall quality of the spray. Gormley et al. give a thorough description of the relevant physical parameters influencing the performance of water-containing hair sprays¹.

Next to formulating problems, the performance of the system in the final product is the most critical issue, especially for the consumer. As higher levels of water in the spray lead to increased drying times, the consumer will notice a difference from traditional high VOC-products. More than that, as water has a high density and evaporates slowly, it can partially destroy the hairstyle simply by its own weight. The hair itself is composed of proteins that form a higher-order upper structure by building hydrogen and ionic bonds between adjacent protein chains, which are, apart from the cystine-bonds, responsible for the stability of the hair itself and the style retention. In

humid conditions, these bonds break and destabilize the hair set structure, which leads to a slight straightening of the hairstyle. When a spray with high water content is applied to the hair, some of the hair's hydrogen bonds break and the initial curl retention decreases (curl droop). This is the main reason why high water hairsprays do not maintain a style as well as the traditional anhydrous systems.

To help solve problems linked to low-VOC formulations, polymer suppliers have developed new resins, which are well suited to meet the challenge of 55% VOC hairsprays. These include emulsion polymers such as **BALANCE[®] CR** polymer or **BALANCE[®] 0/55** polymer (INCI: Acrylates Copolymer), as well as **BALANCE[®] 47** polymer (INCI: Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer) and the new **DynamX[®]** styling polymer (INCI: Polyurethane-14 (and) AMP-Acrylates Copolymer) from National Starch Personal Care.

MAJOR CHALLENGES IN FORMULATING LOW VOC HAIRSPRAYS

Shifting formulations from a high-VOC content to 80% VOC was a target easily achieved in the early 1990s, as most polymers and formulations were able to sustain the incorporation of water. Since most of those formulations were capable of tolerating the additional water, no major reformulating was initiated. Only when restrictions on the possible VOC emissions from hairsprays became tighter and CARB imposed a 55% VOC limit on hairsprays by 1999, formulators had to change their formulations. By then, numerous options of preventing an unacceptable deterioration of product performance were identified. Some of those concerns are sprayability, stiffness and can corrosion.

Sprayability and Stiffness

The viscosity of the system primarily influences sprayability, which for a given polymer is a function of its use level and the ratio of ethanol/water. As more water is added to the formulation, the viscosity increases thus making it more difficult to atomize the aerosol. Additionally, the surface tension increases as well, which makes

it more difficult for the polymer-solution to spread on the hair-fiber. Both effects are shown in diagram 1.

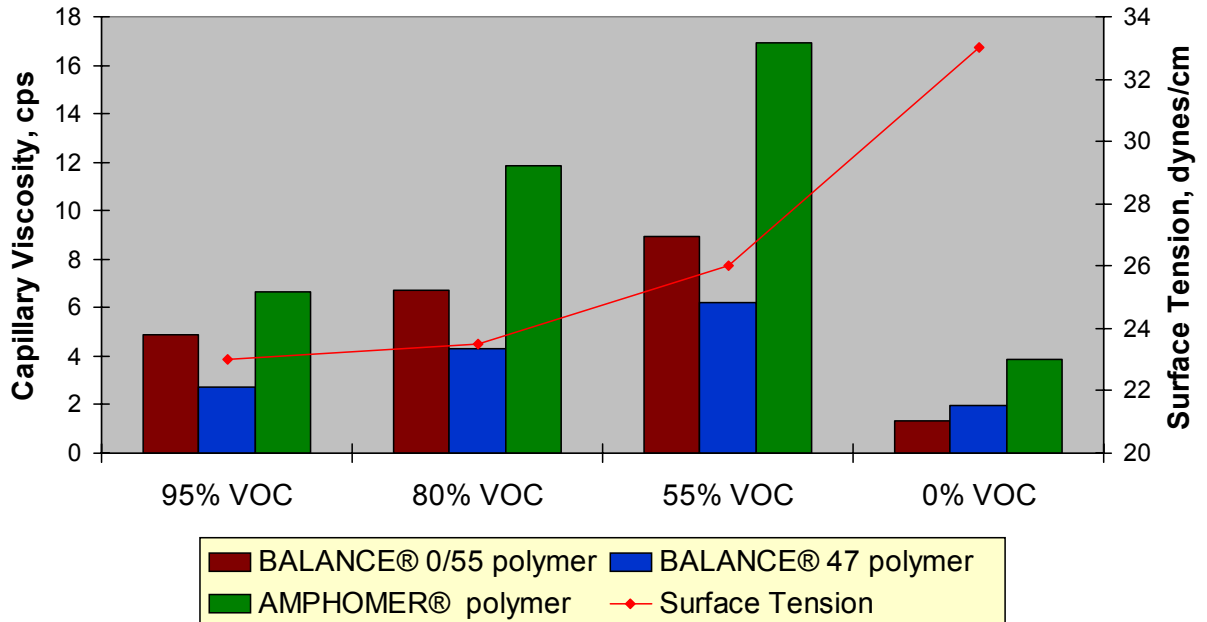


DIAGRAM 1: Effect of VOC Level and Polymer-Type on Viscosity and Surface Tension (5% Polymer solution)

Traditional hair spray polymers with their high molecular weights have high viscosities in water, making them hard to spray. The higher surface tension of water also contributes to poor wetting and wicking (flow along the hair). After spraying, the polymer is not carried well to points where hair fibers intersect, leading to poor bonding. This again leads to lack of desired stiffness and hold.

Therefore, lower-viscosity polymers; such as emulsion polymers like **BALANCE® 0/55** polymer (INCI: Acrylates Copolymer) and dry-powder polymers such as **BALANCE® 47** polymer (INCI: Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer) were introduced. These polymers have lower molecular weights (20.000 to 50.000 as compared to > 150.000), which also could lead to lower overall hold of the final hairspray, due to lower hair-polymer-hair bond toughness.

Therefore just switching to another polymer does not resolve the issue of reformulating. As we have seen, sprayability is influenced by viscosity, but as hold and stiffness are usually a function of molecular weight, a feasible compromise has to be found. One option is to blend polymers of lower and higher molecular weight to get

the desired sprayability and stiffness. This gives the formulator the option of fine-tuning the desired properties. Also the total amount of water has an influence on the way the hairspray performs. Preferably, the water has to be driven down to a minimum. Due to its physical parameters, water evaporates slowly and additionally breaks some of the hydrogen bonds between adjacent proteins within the hair, causing a curl droop. One way of preventing curl droop is to raise the amount of polymer, as this will lead to an overall performance boost (to compensate for the curl droop caused by the water) and will lower the total water content as well.

To attain the best of both worlds (low viscosity and higher hair-polymer-hair bond toughness), **DynamX[®]** styling polymer was developed. The polyurethane functionality of this product allows it to form tough bonds even though it is a low molecular weight polymer, delivering excellent overall on-hair performance.

Even though sprayability and particle size can be influenced by the right choice of polymers, more additives are needed to further optimize the system. Certain silicones are well known to improve performance of high-VOC hairsprays. Some of these also are well suitable to reduce particle size in low-VOC water containing hairsprays, such as Cyclomethicones and Dimethicone Copolyols.

Diagram 2 shows the influence of various silicones on the particle size of a given 55% VOC aerosol.

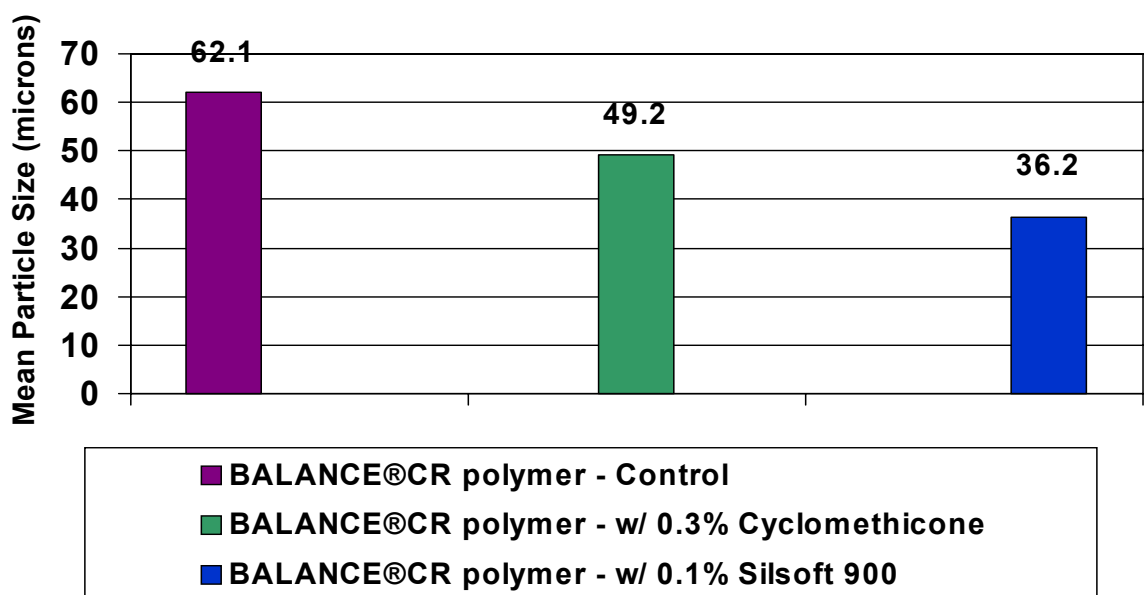


DIAGRAM 2: Influence of additives on particle size of a 55% VOC hairspray (5% polymer solids, water/EtOH/DME, aerosol system)

Depending on the right choice of additives, the particle size can be decreased. The incorporation of silicones will lead to improved sprayability and the option to increase solids, thus delivering better hold. Furthermore, silicones will reduce the surface tension of the system, which by itself gives better wetting of the hair fiber. If the fiber is well wetted by the polymer solution, the flow along the fiber (wicking) takes place at a higher pace, which in turn leads to better bonding at the intersects of hair fibers, resulting in better stiffness and hold.

Can corrosion

As low VOC aerosol hairsprays may contain up to 40% water, corrosion of the packaging is a serious issue as well, which needs to be addressed. The ionic properties of a typical water-based 55% VOC formulation can lead to can corrosion, especially in tin-plate cans. While some additives like surfactants may contribute to on-hair performance, they amplify corrosion in the can. Aluminum containers usually are not prone to corrosion at about neutral or low pH, but often the cost constraints prohibit their usage and tin-plate cans are the only option. If that is the case, the formulation has to be carefully checked for corrosion. Next to using corrosion resistant resins, such as **BALANCE[®] CR** polymer (INCI: Acrylates Copolymer) from National Starch, there are additional ways to limit corrosion. First of all, the total water content should be as low as possible (higher polymer solids, increased amount of propellant). As a second option, a variety of corrosion inhibitors can be used (Sodium Benzoate, Ammonium Benzoate, Cyclohexylamine).

In conjunction with the control of the total ion content, this usually leads to stable formulation.

Exemplary Formulations

With the above details in mind, basic low-VOC starting formulations are discussed and compared to high-VOC aerosol hairsprays.

The following formulations are low, medium and high VOC formulations, based on an acrylic resin. The 55% formulation used hydrofluorocarbon 152a, which is exempt from the VOC legislation in the USA making this actually anhydrous hairspray a 55% compliant formulation. The 80% VOC formulation represents a spray, which is similarly formulated to standard high VOC aerosols.

Ingredient	INCI	Anhydrous 55% VOC (8409-85D)	80% VOC (7055-32)	Anhydrous High VOC (12680- 57D)
AMPHOMER® 4910	Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer	4	6.5	5
AMP-95	Aminomethyl Propanol	0.7	1.07	0.92
Silsoft A843 *)	Bisamino PEG/PPG-41/3 Aminoethyl PG-Propyl Dimethicone	0.1		
DC 193 Surfactant *)	PEG-12 Dimethicone			0.5
SD Alcohol 40	Alcohol denat. (SD Alcohol 40)	55	50	53.58
Deionized Water	Aqua (Water)		12.43	
Dymel 152 A *)	Hydrofluorocarbon 152	40.2		
DME	Dimethylether		30	40
		100	100	100

The above formulations are characterized by their hard holding properties, derived from the acrylic polymer. The 55% spray based on hydrofluorocarbon 152a performs similar to high VOC spray, as it contains no water, which would affect the performance.

The following examples demonstrate the effect how the increase in viscosity can be minimized when going from a high to a low VOC system. The examples are based on a vinyl acetate copolymer. Shifting this system to a low-VOC formulation the total solids are increased (from 5% to 5.5%), but the level of the high molecular weight Vinyl Acetate polymer is reduced and compensated with a lower molecular weight acrylate. This combination leads to good sprayability and good on-hair performance. The acetone used as co-solvent (which is also exempt from being a VOC by the US-legislation) additionally helps to improve sprayability, reduces particle size and allows for quicker drying times.

Ingredient	INCI	55% VOC (9747-71)	High VOC (12680-36B)
BALANCE [®] CR (45% solids emulsion)	Acrylates Copolymer	5.45	
RESYN [®] 28-2930	VA/Crotonate Vinyl Neodecanoate Copolymer	3	5
AMP-95	Aminomethyl Propanol	0.67	0.52
Citroflex-2 *)	Triethyl Citrate	0.25	
Sodium Benzoate	Sodium Benzoate	0.25	
DC 193 Surfactant *)	PEG-12 Dimethicone		0.5
SD Alcohol 40	Alcohol denat. (SD Alcohol 40)	22	43.98
Acetone	Acetone	7	
Deionized Water	Aqua (Water)	28.38	
DME	Dimethylether	33	40
CAP 40	Propane/Butane (app. 2.8 bar)		10
		100	100

Other 55% VOC-examples are based on acrylate technology, using either a higher solid content (8757-118-5) or a combination of a traditional high-VOC, high molecular weight polymer with a low-VOC, low molecular weight polymer (8409-95E) to achieve the desired on-hair performance. Both formulations provide good hold and humidity resistance while also having excellent spray aesthetics.

Ingredient	INCI	55% VOC (8409-95E)	55% VOC (8757-118-5)
BALANCE [®] 47	Octylacrylamide/Acrylates/But ylaminoethyl Methacrylate Copolymer	4	
AMPHOMER [®] 4910	Octylacrylamide/Acrylates/But ylaminoethyl Methacrylate Copolymer	1	
BALANCE [®] CR (45% solids emulsion)	Acrylates Copolymer		14
AMP-95	Aminomethyl Propanol	0.97	0.84
GE Silicones SF 1204 *)	Cyclomethicone	0.6	
Silsoft 900 *)	PPG-12 Dimethicone		0.05
SD Alcohol 40	Alcohol denat. (SD Alcohol 40)	22	22
Deionized Water	Aqua (Water)	38.43	30.11
DME	Dimethylether	33	33
		100	100

Further examples are based on urethane-technology, demonstrating the possibility to formulate low- and high-VOC hairsprays with this new polymer material. Regardless of VOC-level, the low viscosity of DynamX styling polymer leads to good spray atomization and fast drying times. In combinations with other acrylic resins, additional stiffness can be achieved.

Ingredient	INCI	55% VOC Style Look Hairspray (12774-09B)	55% VOC Durable Hold Hairspray (12774-09A)	High VOC Style Memory Hairspray (12680-57H)
DynamX® (28% active)	Polyurethane-14 (and) AMP-Acrylates Copolymer	14.28	17.85	3.57
AMPHOMER® 4910	Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer			4
AMPHOMER® LV-71	Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer	1		
AMP-95	Aminomethyl Propanol	0.2		0.73
Silsoft A843 *)	Bisamino PEG/PPG-41/3 Aminoethyl PG-Propyl Dimethicone	0.05		
Silsoft 900 *)	PPG-12 Dimethicone	0.05	0.05	
DC 193 Surfactant *)	PEG-12 Dimethicone			0.5
Citroflex-2 *)	Triethyl Citrate		0.15	
dl-Panthenol	Panthenol	0.05		
SD Alcohol 40	Alcohol denat. (SD Alcohol 40)	18.43	17.54	51.2
Deionized Water	Aqua (Water)	32.94	31.41	
DME	Dimethylether	33	33	40
		100	100	100

*) Silsoft and GE Silicones are products marketed by GE Silicones/OSI Specialities, Dymel is a tradename of the E.I. Dupont De Nemours Company, DC 193 Surfactant is marketed by the Dow Corning Cooperation, Citroflex is marketed by Morflex Inc.

SUMMARY

In this communication the most important challenges of formulating low-VOC aerosol hairsprays were identified. Issues such as sprayability, hold, on-hair performance and can corrosion were discussed and possible ways to diminish the problems were shown.

As the high water content in low VOC sprays leads to an increase in viscosity, this increase needs to be tackled. Various options to do this include using lower molecular weight polymers, which by themselves contribute less to building viscosity. However, hold and stiffness is usually linked to the molecular weight of the fixative used, and therefore, on-hair performance may suffer by just switching polymers. The formulator may use a combination of polymers to balance on-hair performance versus sprayability as well as incorporating various additives into the hairspray. These additives include silicone-derivatives and surfactants, which help decrease the viscosity as well as reduce the surface tension of the polymer solution, promoting the wetting of and flow on the hair fiber. Alternatively, new polymer technologies, such as polyurethanes, allow the formulator to achieve excellent sprayability, hold, and style memory.

Basic starting formulations are discussed which demonstrate the variety of possible options to design suitable low VOC aerosol hairsprays.

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Contact details:

Dr. Matthias Pfaffernoschke

National Starch Personal Care (Europe)

Industriestr. 17a

CH-6203 Sempach Station, Switzerland

Email: Matthias.Pfaffernoschke@nstarch.com

¹ J.L. Gormley, G.T. Martino, J.G.L. Pluyter, Q.K. Tong; Using Physical Measurements to Optimize Water-Containing Aerosol Hair Sprays., *Cosmetics & Toiletries Manufacture Worldwide*, 1997, 209-216