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# European Hairspray Formulations:
# A Review of Options to Meet a Variety of Consumer Needs

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With the end of CFC use in Europe and the need for better holding hairsprays, a major reformulation effort has taken place in European hairspray products in the outgoing 20th century. While sprays used to be based on PVP and its derivatives, this reformulation led to the incorporation of various other polymer chemistries. Furthermore, not all technologies that worked with CFCs as propellants were feasible with modern propellants such as propane/butane blends and dimethylether. Due to the combination of these factors, acrylate and acetate based technologies became and continue to be the leading polymer technologies in hairsprays today.

Besides these factors, other historical frames need to be considered to understand today's hairspray segmentation throughout Europe, one of them being alcohol taxes. The high taxation of ethanol in Germany and to a lesser extent in France and Italy, meant that reducing the alcohol content by increasing the propellant level could lead to considerable cost savings. Subsequent rationalization of alcohol taxes within the EU reduced the need to do this but the consumer preferences in these countries for high propellant levels and dry hairspray products had been established by then. The result was that although propellant levels decreased, they still remained high in comparison to those member states where the alcohol taxes had traditionally been low (e.g. the UK).

Also, as formulators faced the challenge of overcoming the ethanol tax in different ways (e.g. through the usage of isopropanol) certain brand images were born. As usage of non-taxed solvents was one option to avoid taxation, wetter and drier hairsprays began to coexist in the same market. The usage of solvents other than ethanol and the tendency to increase the propellant level created a variety of polymer technologies in the market place, each designed to address all these needs. Nowadays, basically all hairsprays are based on ethanol and possibly some water (either coming from the ethanol or being specifically added to accommodate solubility

and to adjust drying times). In rare cases, isopropanol and even rarer methylene chloride is used together with ethanol.

Today, formulations can be grouped by regions within Europe and outside as well. The differences in hairspray formulations outside Europe are mainly due to regulatory issues (e.g. low VOC sprays in the USA) and consumer needs, such as hold levels (Asia), leading to different solid levels in hairsprays throughout the world. Within Europe, different polymer technologies are utilized (e.g. acrylates in Germany and vinyl acetates in France).

In order to address the various formulation needs throughout the world, fixative suppliers have developed a wide variety of polymers to satisfy differing needs, ranging from high performance to cost effective choices that deliver optimal quality. National Starch Personal Care offers a wide range of products including acrylate based polymers from the AMPHOMER® polymer and BALANCE® polymer family for stiff, hard holding sprays, vinyl acetate polymers from the RESYN® polymer family provide a desirable feel, as well as the **DynamX®** styling polymer, a polyurethane for achieving flexible, memory-like hold. A summary of available polymers is given in table 1.

Table 1: National Starch Hairspray Polymers

| Trade name | INCI designation | Primary Applications |
|---|---|---|
| **Acrylates** | | |
| AMPHOMER® | Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer | High VOC hairspray, best curl retention, good DME tolerance |
| AMPHOMER® 4961 | Acrylates/Octylacrylamide Copolymer | High VOC hairspray |
| AMPHOMER® LV-71 | Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer | High and 80% VOC Hairsprays |
| | | |
| AMPHOMER® HC | Acrylates/Octylacrylamide Copolymer | High VOC hairspray, especially designed for high levels of propane/butane sprays |
| RESYN® XP | Acrylates/Octylacrylamide Copolymer | High VOC hairspray, highest propane/butane tolerance of all NSC resins |
| **LOW-VOC Acrylates** | | |
| BALANCE® 0/55 | Acrylates Copolymer | 55% VOC sprays, emulsion polymer |
| BALANCE® 47 | Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer | 55% VOC sprays,low viscosity polymer |
| BALANCE® CR | Acrylates Copolymer | 55% VOC sprays, emulsion polymer |
| **Polyurethane** | | |
| **DynamX®** | Polyurethane-14 (and) AMP-Acrylates Copolymer | Flexible Hold sprays that provide long lasting hold, all VOC levels |
| **Vinyl Acetates** | | |
| RESYN® 28-1310 | VA/Crotonates Copolymer | High VOC hairsprays, moderate hold and curl retention |
| RESYN® 28-2930 | VA/Crotonates/Vinyl Neodecanoate Copolymer | High VOC to 55% VOC levels; in low VOC, often used in combinations, nice feel |

Lets take a closer look at the above polymers, discuss where they are used, and why. An overall summary of the different polymers designed for high VOC systems is given in table 2.

Table 2: Summary of Polymer Properties

| Product | Chemistry | Hydrocarbon Propellant Tolerance* | Dimethyl Ether Propellant Tolerance* | Stiffness (comparison at same polymer level) | High Humidity Curl Retention | Notes |
|---|---|---|---|---|---|---|
| **AMPHOMER®** | Acrylate | 40% at 3% polymer | 45% at 3% polymer | High | 80-95% | Excellent stiffness, high humidity curl retention, good compatibility in hydrocarbon and DME systems |
| **AMPHOMER® HC** | Acrylate | 47% at 3% polymer | 40% at 3% polymer | High | 80-95% | Increased hydrocarbon propellant tolerance over AMPHOMER but reduced DME propellant tolerance, excellent stiffness & high humidity curl retention |
| **RESYN XP** | Acrylate | 60% at 2.5% polymer | Currently untested Expected to be less than 40% at 2.5% polymer | Medium High | 80-90% | Cost effective formulations, Excellent on-hair feel, Excellent hydrocarbon propellant tolerance, At use levels greater than 2.5%, wash-off should be tested |
| **RESYN 28-2930** | Vinyl Acetate | 22% at 3% polymer | 50% at 3% polymer | Medium | 70-80% | Good on-hair feel, Good curl retention, Excellent propellant tolerance with DME, Inferior hydrocarbon propellant tolerance |
| **RESYN 28-1310** | Vinyl Acetate | Less than 2930 | 50% at 3% polymer | Medium Low | 60 - 70% | Good on-hair feel, Ok curl retention, Excellent propellant tolerance with DME, Inferior hydrocarbon propellant tolerance |

*Hydrocarbon: Blend AP40, app. 2.8 bar, with following ratio: Propane:IsoButane:n-Butane 22:24:54

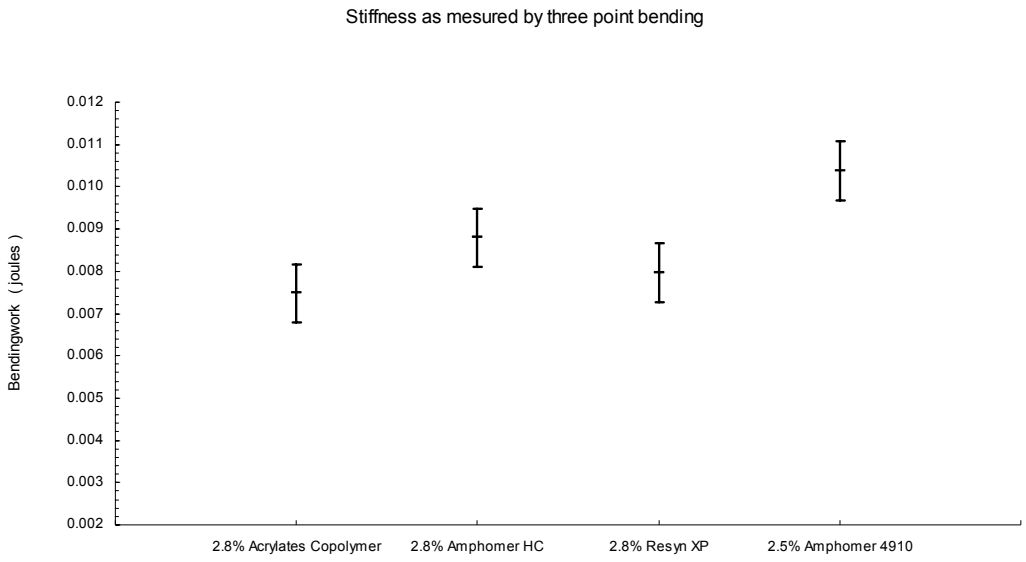
## AMPHOMER® Polymers

The AMPHOMER® polymer family consists of a number of different variants designed for specific applications. While AMPHOMER® polymer is the premium fixative from National Starch Personal Care with the highest overall quality and best feel from an acrylate, AMPHOMER® HC polymer is designed for higher hydrocarbon systems, due to its more hydrophobic character. RESYN® XP polymer takes this concept even further and can be used in cost effective sprays with hydrocarbon propellant use levels of up to 60%. Please refer to table 2 for a close-up look of the product benefits of each polymer.

All three acrylate polymers show very high stiffness (as measured by the three-point bending method). In this test, a spray is applied to a flattened hair swatch and the initial force necessary to bend the hair fibres in measured. As can be seen from

diagram 1, AMPHOMER® polymer outperforms all the others, even at a lower usage level.

Diagram 1, Stiffness of Acrylate Polymers




General Handling

Like all polymers with carboxylic acids groups, acrylates from National Starch Personal Care need to be neutralized with an appropriate base. Bases may be organics such as Aminomethyl Propanol (AMP) or inorganic, such as Potassium hydroxide (KOH). By neutralizing the carboxylic acid groups the polymer becomes water soluble, as this is needed to be able to remove it from the hair with shampoo. Additionally, when neutralizing the polymer, the polymer characteristics, such as stiffness, hold and hardness can be fine-tuned, depending on the base and degree of neutralization chosen. Usually, AMP is the best choice as neutralizer, but in some cases, inorganic bases might be used to provide a stiffer feel on the hair.

Formulating with Different Polymers

AMPHOMER® polymer is one of the leading hairspray polymers and can be found in a variety of different formulations. Its outstanding high humidity curl retention behaviour in conjunction with excellent stiffness and very unique feel attributes make this polymer a favourable choice for many formulators. Many Western European hairsprays are based on AMPHOMER® polymer; however, significant differences in

formulation are seen. In countries where ethanol taxation was low, sprays tend to be rather wet and do not contain as much propellant as in countries where ethanol taxation was high. This has lead to a multitude of formulations, ranging from low levels of propellant (often propane/butane) to very dry sprays with high levels of propellant, typically using dimethylether. However, as the ethanol tax has been abolished for quite some time now, formulations are designed around performance and consumer needs, rather than ethanol content. This means that in geographical regions, different formulations are found.

AMPHOMER® polymer is the premium offering from National Starch Personal Care and can be formulated in a variety of ways. Typically, it is compatible with propane/butane blends of up to 40%, while it tolerates up to 45% DME (at 3% polymer use level). Some examples of traditional hard holding, stiff hairsprays are given in the tables below. Depending on desired properties, such hold and high humidity curl retention, various levels of polymer should be used. Also, particle sizes and discharge rate will influence the hold level as well as the aesthetic properties (spray pattern). To fine-tune these, the formulator needs to adjust the total amount of propellant and in the case of propane/butane, can choose the pressure of the blend as well. Generally speaking, the higher the pressure of the propellant, the finer the spray pattern which could lead to a lower hold level.

| Ingredient | INCI | A | B | C |
|---|---|---|---|---|
| AMPHOMER® | Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer | 5.0 | 3.0 | 5.0 |
| AMP-100 | Aminomethyl Propanol | 0.87 | 0.5 | 0.82 |
| DC 193 Surfactant *) | PEG-12 Dimethicone | 0.5 | 0.3 | |
| DC 556 *) | Phenyl Trimethicone | | | 3.0 |
| Ethanol | Alcohol denat. | 53.63 | 66.2 | 66.18 |
| CAP40 | Propane/Butane | | 30 | 25 |
| DME | Dimethylether | 40 | | |
| | | 100 | 100 | 100 |

*) DC 193 Surfactant and DC556 are marketed by the Dow Corning Cooperation, AMP is supplied by ANGUS (Dow Chemical)

Next to being used on its own in hairsprays, AMPHOMER® polymer can also be used with Vinyl Acetates and Polyurethanes, as indicated in the table below. Formulations with RESYN® 28-2930 polymer tend to be less raspy in feel, due to the vinyl acetate component of the polymer. The formulation with **DynamX®** polymer on the other

hand delivers a flexible hold hair spray, with improved durability, as needed for today's long lasting performance products. **DynamX**® polymer can be used at various ratios with AMPHOMER® polymer, where the flexibility benefits increase with higher ratios of **DynamX**® polymer used. (see also ASAP 1/2004, "Flexible Hold Hairsprays with Long-lasting Performance").

| Ingredient | INCI | D | E |
|---|---|---|---|
| RESYN® 28-2930 | VA/ Crotonates /Vinyl Neodecanoate Copolymer | 2.0 | |
| AMPHOMER® | Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer | 2.0 | 4.0 |
| **DynamX**® (28% active) | Polyurethane-14 (and) AMP-Acrylates Copolymer | | 3.57 |
| AMP-100 | Aminomethyl Propanol | 0.57 | 0.69 |
| DC 193 Surfactant *) | PEG-12 Dimethicone | 0.50 | 0.5 |
| Ethanol | Alcohol denat. | 54.93 | 51.24 |
| CAP40 | Propane/Butane | 24.0 | |
| DME | Dimethylether | 16.0 | 40.0 |
| | | 100.0 | 100.0 |

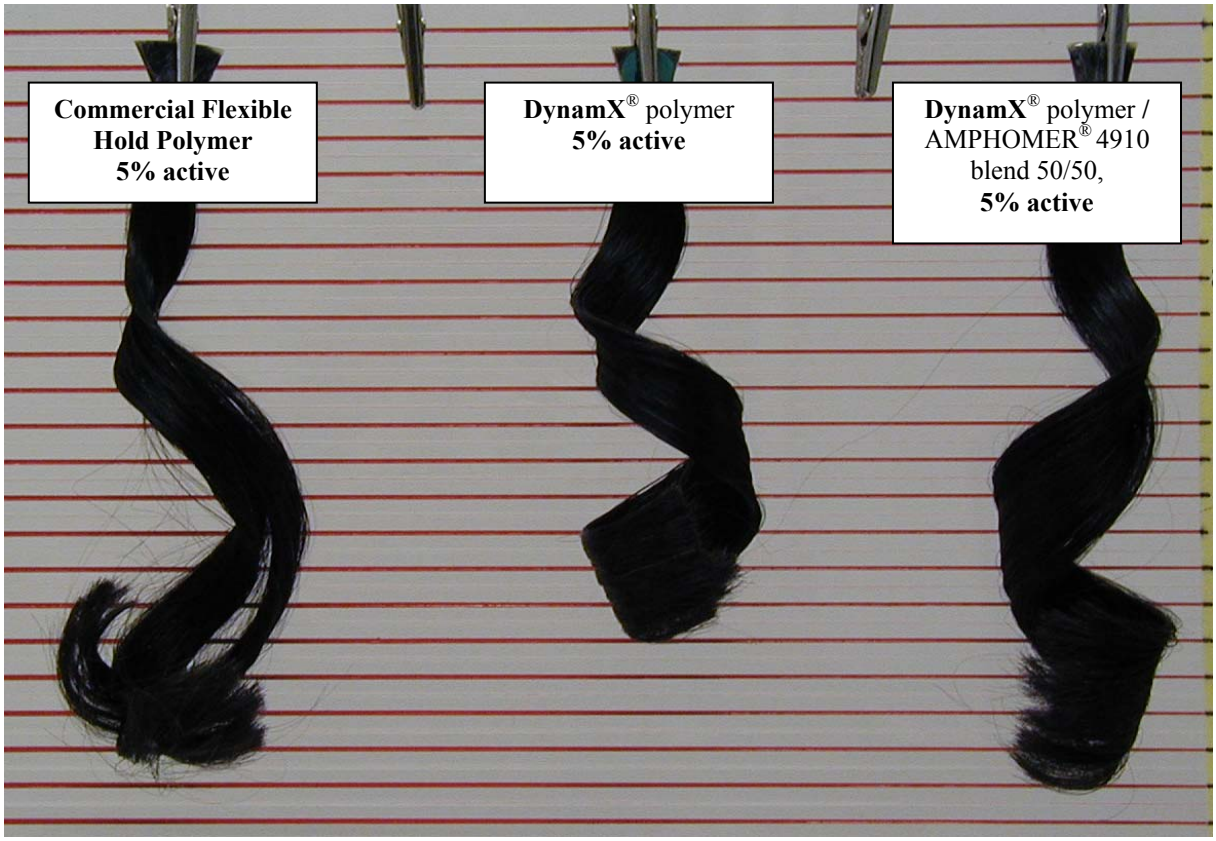
*) DC 193 Surfactant is marketed by the Dow Corning Cooperation, AMP is supplied by ANGUS (Dow Chemical)

As mentioned earlier, acrylates tend to give stiff, hard holding hairsprays, which do not suit all markets and consumer needs. Therefore they can either be used in combination with other polymers, or the amount of plasticizer (e.g. silicones) must be increased. Using too much silicone can decrease the cloud point of a formulation, making it necessary to reduce the total propellant level or even the solids level.
An alternative is the usage of flexible polymers, such as **DynamX**® polymer. This urethane based chemistry gives very durable hold and reduces frizz of the hair. As the urethane on its own leads to very soft films, which some consumers perceive as no fixation power, a blend of **DynamX**® polymer with e.g. AMPHOMER® polymer could be a suitable solution. Depending on the desired flexibility and/or stiffness, the ratio between the two can be chosen anywhere from 0-100, but it is recommended to use at least 15-20% **DynamX**® polymer of the total polymer solids. Otherwise, the durability and flexibility is not perceivable. This is shown on below diagram, where hair tresses have been sprayed with aerosol hairsprays based on 5% polymer. Then a mechanical stress was applied to the tresses (the swatches were pulled 25 times

between two fingers), simulating wind and other environmental conditions, causing a hair-set to deteriorate.

As can be seen, the **DynamX®** polymer as well as the swatch with the **DynamX®** polymer / AMPHOMER® polymer blend perform quite well against the mechanical stress, demonstrating good durability and hold, even after being subject to severe conditions (details of the durability test can be found in the appendix).

Diagram 2: Results of Durability Test




Hair tresses treated with DynamX polymer result in superior durability and reduced frizz compared to commercial flexible hold products.

Cost Effective Hairspray Formulations

In areas and applications, where higher levels of propane/butane are needed, AMPHOMER® HC polymer and RESYN® XP polymer are the more suitable polymers offered by National Starch Personal Care. While AMPHOMER® polymer can be used with propane/butane up to 40%, AMPHOMER® HC polymer pushes this limit up to 45% and RESYN® XP polymer may be used in formulations with up to 60% propane/butane (refer also to table 2). This is achieved by incorporating more hydrophobic monomers into the polymer, making these polymers more tolerable to apolar hydrocarbons.

The possibility to formulate with higher levels of propellant makes both polymers very well suited for low cost market segments, such as private label brands and some Eastern European brands, where margins are under constant pressure.
Some examples of typical formulations with RESYN® XP polymer and AMPHOMER® HC polymer are given in the table below.

| Ingredient | INCI | F | G | H |
|---|---|---|---|---|
| AMPHOMER® HC | Acrylates/Octylacrylamide Copolymer | 3.0 | | |
| RESYN® XP | Acrylates/Octylacrylamide Copolymer | | 2.0 | 2.5 |
| AMP-95 | Aminomethyl Propanol | 0.76 | 0.41 | 0.51 |
| DC 193 Surfactant*) | PEG-12 Dimethicone | 0.2 | 0.1 | |
| DC 345 Fluid | Cyclomethicone | 0.1 | 0.1 | 0.1 |
| Ethanol | Alcohol denat. | 50.94 | 37.39 | 46.89 |
| CAP40 | Propane/Butane | 45.0 | 60.0 | 50.0 |
| | | 100.0 | 100.0 | 100.0 |

*) DC 193 Surfactant is marketed by the Dow Corning Cooperation, AMP is supplied by ANGUS (Dow Chemical)

Vinyl Acetate Polymers

Chemistries other than acrylates are also available and can be found in a number of hairsprays and all European markets. When comparing hairsprays based on vinyl acetate vs. acrylate chemistries, the two major differentiators are high humidity curl retention and feel. Formulas based on vinyl acetate copolymers tend to provide moderate curl retention performance, but provide a smooth, soft feel when compared to traditional acrylate-based formulas. The offerings from National Starch Personal Care are, RESYN® 28-2930 polymer and RESYN® 28-1310 polymer, both VA/Crotonates Copolymer, where RESYN® 28-2930 polymer is hydrophobically modified with vinyl neodecanoate monomer to achieve better high humidity curl

retention results. While both polymers have good DME tolerance, the tolerance towards propane/butane is quite limited in the 20-30% range, depending on polymer solids. In high VOC systems, it is used on its own or in blends with acrylates, depending on the desired feel/hold properties (see also formulation D). RESYN® 28-2930 polymer is also commonly used in Low VOC 55% aerosol hairspray systems in the United Stated, often in combination with low molecular weight acrylates such as BALANCE® 47 polymer or BALANCE® CR polymer (see also ASAP 1/2005, Formulating Low VOC Aerosol Hairsprays).

In European high VOC aerosol sprays, the sensory benefits of the vinyl acetate are the key reason to choose RESYN® 28-2930 polymer over AMPHOMER®-type polymers, as the feel of the polymer film is different. Examples of typical formulations are given below.

| Ingredient | INCI | I | J | K |
|---|---|---|---|---|
| RESYN® 28-2930 | VA/ Crotonates /Vinyl Neodecanoate Copolymer | 2.25 | 4.5 | 5.0 |
| AMP-95*) | Aminomethyl Propanol | 0.21 | 0.42 | 0.52 |
| DC 193 Surfactant*) | PEG-12 Dimethicone | 0.5 | 0.3 | 0.5 |
| Ethanol | Alcohol denat. | 67.04 | 74.83 | 51.24 |
| CAP40 | Propane/Butane | 30.0 | 20.0 | 10.0 |
| DME | Dimethylether | | | 40.0 |
| | | 100.0 | | 100.0 |

*) DC 193 Surfactant is marketed by the Dow Corning Cooperation, AMP is supplied by ANGUS (DOW CHEMICAL)

Summary

This article described the various high VOC aerosol hairspray formulations, based on National Starch polymer technology. Different polymers are used in a multitude of formulations, covering many formulators' needs. Stiff hard holding sprays based on AMPHOMER® polymers as well as flexible hold sprays using **DynamX**® polymer are described. Propellant level can reach up to 60% to make very cost effective and dry hairsprays. Choosing from the multitude of options, picking the right polymer to satisfy the consumer's needs is the formulators' skill. Polymers from National Starch Personal Care help provide a wide variety of hairspray formulation options for all regions of the globe.

Appendix

**Durability Test Method**

Dynamic Curl Memory, a subjective test, has been developed in order to evaluate the hairspray's ability to resist deformation and return the hair to its original style (memory). In this test, 25 cm hair tresses are rolled on a hot iron to set an initial curl. The curled swatches are then sprayed and allowed to dry for one hour. The dry, treated swatches are hung on retention boards (at 21 °C and 50% relative humidity (RH)) and initial readings are taken. The swatches are then pulled by running the index finger down the swatch, extending it the full 25 cm and releasing, allowing the swatch to spring back into place. The swatches are challenged a total of 25-30 times with readings being taken at 1, 5, 10, 15, 20, 25 and 30 pulls. The data are then statistically analyzed and reported at a 90% confidence level as percent retention. The higher the retention values, the better the swatch bounces back into place, indicating good memory and stable bonds holding the individual hair fibers together.

For more information about National Starch Personal Care products, please visit www.personalcarepolymers.com

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