Product Label Analysis Project
Submitted for Chemistry 503, 2005/6

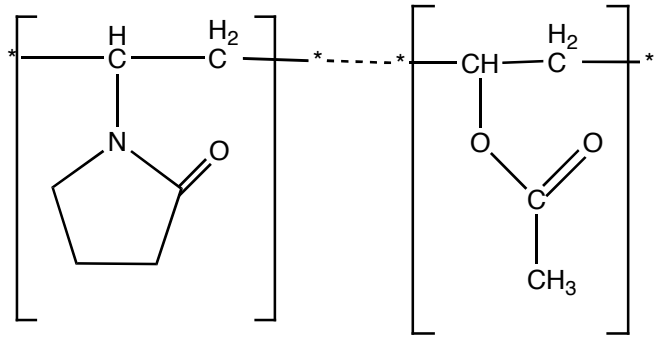
Hair Volumizers and Thickeners

As someone who has been in battle with their hair texture for many decades, I have welcomed the advances made by chemists in the cosmetic industry and the avalanche of hair care products now available on the market. Curly hair now can be straightened, shine added to what was once dull, unmanageable mops now can be managed, and those of us born with flat, thin, limp hair but dying to have the hair of a diva now have a choice of many hair care products which promise to produce our desired look. We have hairspray, gels, mousse, and finally, with the chemical advances made in polymer chemistry, volumizers and hair thickeners. Volumizers and hair thickeners are applied to the roots and hairline of damp hair, which is then blown dry.

The following analysis will take a look at the structure, chemical properties and role of several of the chemicals in six hair thickener and volumizing products. The products used for this analysis are Bb Thickening Spray, Bb Styling Spray, Sebastian Double Body Thickefy Styler, Pureology Pure Volume Blowdry Amplifier, Paul Mitchell Volumizing Spray, and Nexxus Volumizing Foam Styler. All six products are higher end hair care products and can only be purchased at professional beauty salons, resulting in a much higher price tag. Some chemicals appear in several products, others in only one or two. Similar types of products were chosen to compare and contrast ingredients. A complete list of ingredients for each product appears in Appendix I.

Common to all products is PVP/VA Copolymer, which acts as a hair-fixing agent.

Chemical Structure: PVP/VA Copolymer

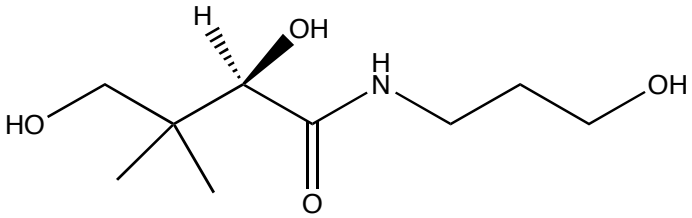


PVP, polyvinylpyrrolidone, was one of the first polymers used in hair styling products but, because it is water-soluble and absorbs atmospheric moisture, it becomes sticky and is not a very suitable hair fixative by itself. VA, vinyl acetate, is insoluble in water but dries to a brittle film. Manufacturers formulate PVP/VA Copolymer with various ratios of PVP to VA ranging from 70:30 to 30:70 depending upon the desired properties of the hair fixative product as well as the desired viscosity of the product. It is a nonionic polymer and establishes elastic links between single hairs. These elastic links allow the hair to flow with a natural look while still holding the style. It is easily washed out of hair. PVP/VA copolymer is also used as a remoistenable adhesive, a viscosity-enhancing agent

and protecting colloid for printing ink, a binder in coatings, a stabilizer for the dispersion of dyes, and as a film coatings agent in the pharmaceutical industry.
Interestingly, there is no other specific ingredient that is common to all six products although several ingredients used in more than one product are similar in chemical structure and function.

Panthenol is an ingredient in three products, the Sebastian Thickefy Styler, Pureology Pure Volume Bowdry Amplifier, and Paul Mitchell Volumizing Spray. It is the alcohol analog of pantothenic acid (Vitamin B3), very soluble in water, alcohol and propylene glycol due to the three OH groups, soluble in ether and chloroform, and slightly soluble in glycerin.

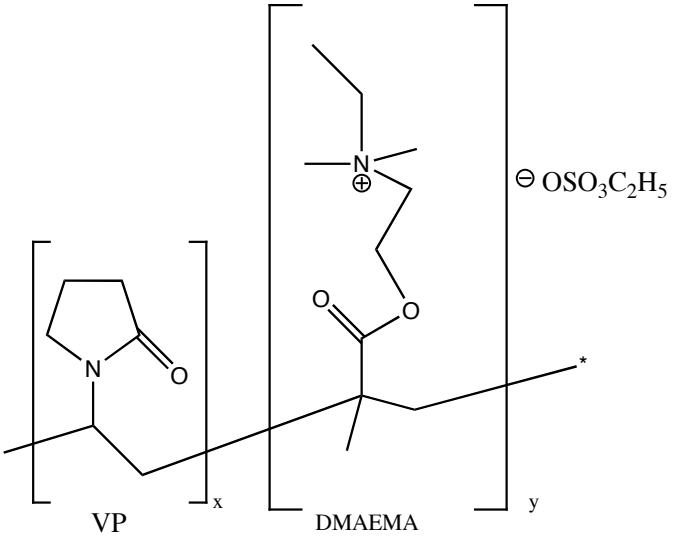
Chemical Structure: Panthenol



Panthenol comes as two enantiomers and for cosmetics is either in d form or as a racemic mixture of d and l. It binds to the protein in the hair follicles, coating the hair, strengthening its structure and sealing its surface, making them appear shiny, as well as forming a moisturizing coating. It is usually present in concentrations of 0.1 – 1%. Panthenol is also used in pharmaceutical ointments and creams used for treating minor skin disorders, sunburns and burns.

Four of the six products contain one or more types of quaternary ammonium salts including Polyquaternium-4, Polyquaternium-7, Polyquaternium-11, Polyquaternium-26, and Polyquaternium-37. Polyquaternium-11 will be specifically discussed here and is also known as Quaternium-23. Quaternary ammonium salts have four alkyl bonds to a nitrogen atom.

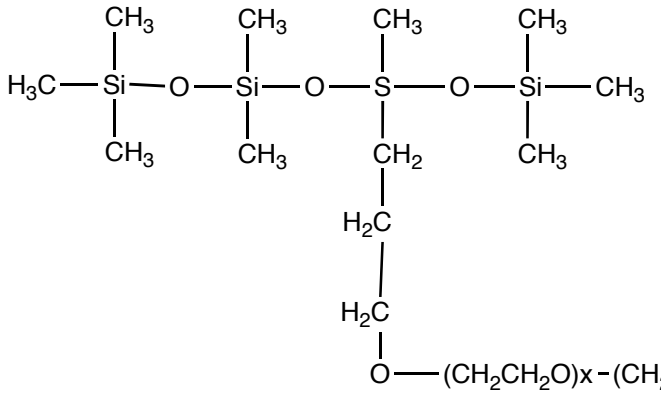
Chemical Structure: Polyquaternium-11



Polyquaternium-11 is a quaternized copolymer of vinyl pyrrolidone (VP) and dimethylaminoethyl methacrylate (DMAEMA) in aqueous solution. It is 67% VP by weight and 33% DMAEMA by weight. It improves the wet combability of the hair and prevents electrostatic charging when hair is dry due to its high cationic charge on the nitrogen. It binds and forms a shield around each hair to protect its surface from attack. Polyquaternium-11 is especially recommended for styling products such as mousse, lotions, and conditioning rinses due to its high molecular weight and specific composition providing a good setting effect. The setting effect is determined by a numerical scale of hair stiffness based on 2.2% polymer content and 65% relative humidity. Quaternary-26 is used as film former, hair conditioning agent, and antistatic agent in a variety of cosmetic products. Polyquaternium-4 also enhances combing as well as adds conditioning and sheen to hair. Polyquaternium-7 is derived from lauric acid, a common constituent of vegetable fats, especially coconut oil and laurel oil. It is used for its foaming properties and as an antibacterial agent. Polyquaternium-37 is also a film forming agent and conditions and improves styling hold and elasticity of the hair. There is a difference in terms of the absorbance of these polymers on the hair. For example, Polyquaternium-10 (not present in these products) is the only polymer of this type that could be desorbed from the hair by rinsing with water/surfactant. The reason for this is that it is a branched polymer and therefore is more coiled than a linear polymer like Polyquaternium-7. It is therefore less hydrated, less strongly adsorbed on the hair than a linear polymer and more easily desorbed if necessary. Hair care products containing linear polymers such as Polyquaternium-7 could over condition the hair and cause a build up.

Dimethicone copolyol is a term that describes a class of silicone/polyoxyalkylene derivatives. The name was developed to reflect the molecular structure – a silicone polymer (dimethicone) with a copolymer ("copoly" part) and a hydroxyl functional group (ol ending). It is a copolymer of polydimethylsiloxane and polyoxyalkylene ether. It is a non-ionic surfactant that increases the wetting of hair while enhancing foaming characteristics. Surfactants have a hydrophilic portion (in this case the ether portion with its high dipole moment) and a hydrophobic portion which help to reduce the surface tension of water as well as form bubbles due to the interactions of the hydrophilic and hydrophobic portions of the molecule.

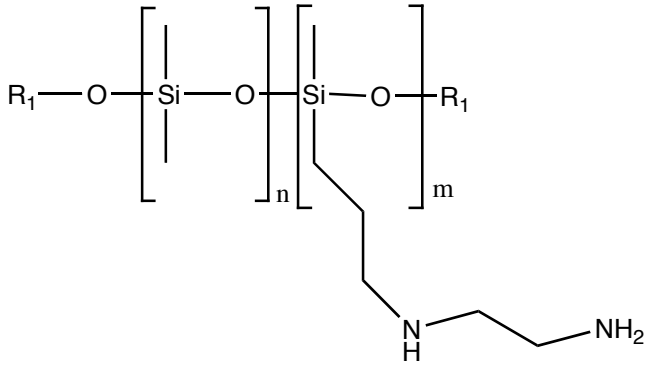
Chemical Structure: Dimethicone copolyol



Amodimethicone is present in two of the products and is a linear, reactive aminofunctional polydimethysiloxane. The amine units under acidic conditions, such as

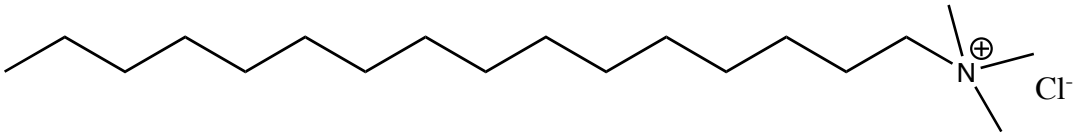
those in a hair care product, are transformed to a cationic ammonium unit making it a cationic polymer with excellent conditioning properties. The reactive, aminofunctional silicone fluid crosslinks upon drying to form a protective sheath around the hair fiber. This protective sheath improves wet and dry combability, increases softness, shine, and static control. The protective sheath will last through several shampoos. Interestingly, there is not a build up of silicone from repeated applications of the hair product because the silicone film itself limits the deposition of active silicone on the hair.

Chemical Structure: Amodimethicone



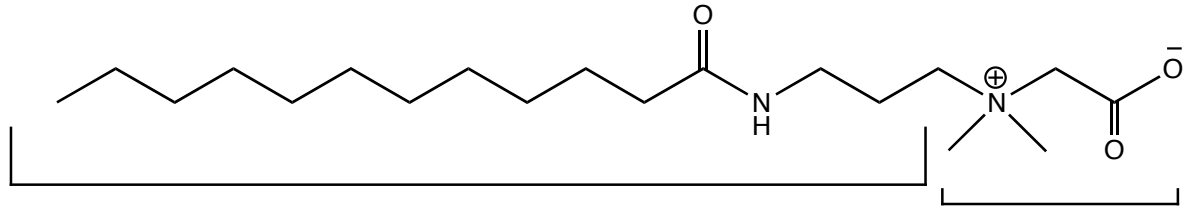
Cetrimonium chloride, a quaternary ammonium compound is present in two of these hair products and is present in hair conditioners, rinses, skin creams and lotions. It is a cationic emulsifier (binds substances together such as oil and water which would not mix) and is water soluble. It conditions hair, resulting in shine and produces good wet and dry combability. It is also used as a softener for textiles. Its positive charge results in antistatic properties in wool, cotton, other cellulose fibers and in certain synthetic fibers.

Chemical Structure: Centrimonium chloride



Of the products examined in this paper, Sebastian Thickefy Styler is the one I use everyday and therefore the one I was most curious about. The third ingredient listed is cocamidopropyl betaine, which is a mild high foaming amphoteric surfactant derivative of cocamide, and betaine. It contains a quaternary ammonium cation as part of its structure.

Chemical Structure: Cocamidopropyl betaine

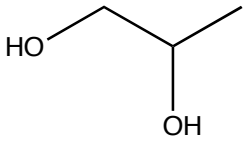


cocamide MEA betaine

This product is dispensed as a foam and cocamidopropyl betaine provides good foaming and foam liquid stabilization again due to having both polar portions (COO^- and R_4N^+) and a nonpolar portion (hydrocarbon chain) in its molecule. Cocamidopropyl betaine has excellent wetting properties and is used to boost and stabilize foam and improve viscosity of the product.

Three of the products including the Sebastian Thickefy Styler contain propylene glycol also known as 1, 2-propanediol. It is a clear, colorless, viscous liquid used as a humectant and solvent. A humectant helps to retain moisture by forming hydrogen bonds with water, thus preventing it from evaporating.

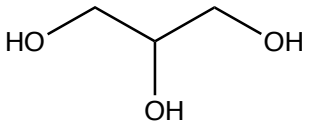
Chemical Structure: Propylene Glycol



Two products contain glycerin, a compound similar to propylene glycol. Glycerin, also known as glycerol or 1,2,3-propanetriol, is colorless, odorless, and hygroscopic and is a sweet tasting viscous liquid. With three hydroxyl groups, it is very soluble in water. It is a bi-product of saponification and the transesterification process to obtain biodiesel, produced by the hydrolysis of three ester linkages and the loss of three equivalents of fatty acid from fat or biological oil.

In hair care products, glycerin serves as a humectant that penetrates the hair shaft. It causes the hair shaft to soften and swell making it more water retentive. In addition, it serves as an emollient to the hair, smoothing it and leaving it free of frizz.

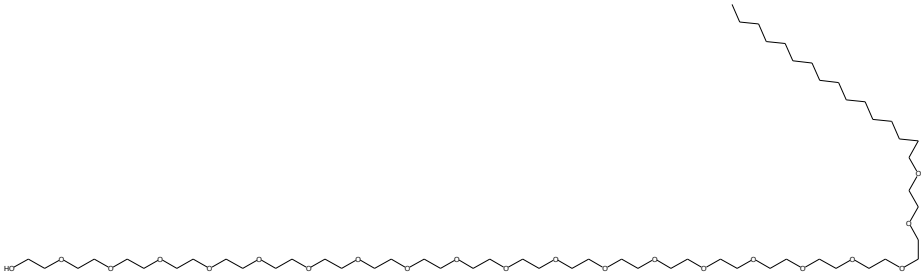
Chemical Structure: Glycerin



Ceteareth-20, also in Sebastian Thickefy Styler, is the polyethylene glycol ether of cetearyl alcohol and is classified as an alkoxylated alcohol. It is also known as Brij 58 or

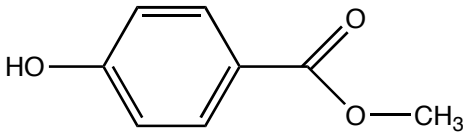
diethylene glycol cetyl ether and has the formula of $C_{56}H_{114}O_{21}$. It is a nonionic surfactant and, with its water-soluble properties as an ether, it is widely used as an emulsifying agent.

Chemical Structure: Ceteareth-20



Parabens, including methylparaben, which is found in four out of six of these hair products, are the most widely used group of preservatives found in cosmetics including facial and body cosmetics, skin care products, hair care products, sunscreens, antiperspirants and deodorants, colognes, perfumes, and soaps. They are effective over a wide range of pH, are derived from plant or petroleum sources, and are effective against bacteria, fungus, yeast and mold, preventing their growth. Methylparaben's primary name is methyl-4-hydroxybenzoate.

Chemical Structure: Methylparaben

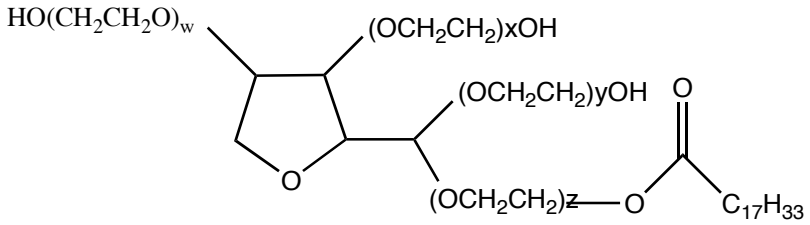


There has been some concern expressed by the natural cosmetic industry and some scientists over the use of parabens particularly in underarm products. A study appeared in the *Journal of Applied Toxicology* in 2004 which was conducted to determined whether any of the six parabens commonly used in consumer products (which included methylparaben) in Europe could be detected in human breast tumors. The study showed that five of the six parabens included in this study were detected intact, meaning they were not changed or metabolized, in human tissues. However, the study did not make any attempt to determine the source of the parabens. It also was not designed to show that any of the parabens caused breast cancer in the women studied. Another study done in 2001 and published in *Food and Chemical Toxicology* does provide evidence that parabens can act as weak environmental estrogens. Additional research must be done to see if exposure to parabens increases the risk of getting breast cancer.

Polysorbate 80, polyoxyethylene sorbitan monooleate, known as Tween 80 and polysorbate 60, polyethylene sorbitan monostearate, known as Tween 60 are ingredients in two of these hair products. They are two members of a series of materials (Tween 20, 40, 60, 80) which are fatty acid esters of sorbitan polyethoxylates. The various Tweens differ in terms of the type of fatty acid present. Tween 80 is an oleate, while Tween 60 is a stearate. They are yellow viscous liquids and act as hydrophilic nonionic surfactants, emulsifiers, and

solubilizers. The molecule has portions that are soluble in water and other portions that are soluble in oil and therefore are good dispersing agents to mix oil and water. Polysorbate 80 can be derived from coconut oil as well as olive oil, while polysorbate 60 is derived from palm oil. I find this a particularly interesting fact because I lived in Malaysia for 14 years, a leading world supplier of palm oil.

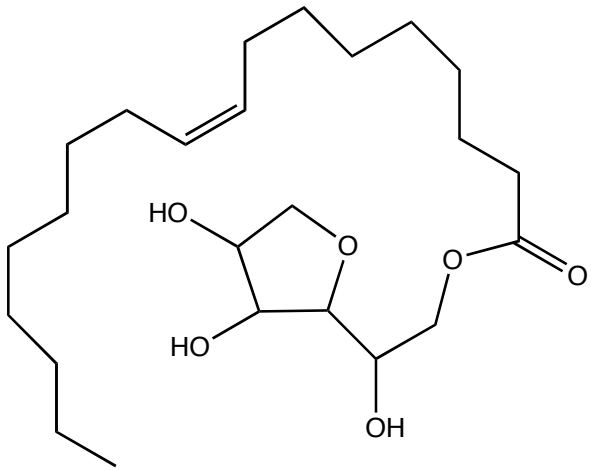
Chemical Structure: Polysorbate 80



Sum of w, x, y, and z is 20

One other product contains sorbitan oleate, also known as SPAN 80. This chemical functions in a similar manner to polysorbate 80 and polysorbate 60. It is found naturally in various berries and fruits. One method for the synthetic preparation of sorbitan oleate involves a two-stage process. In the first stage, sorbitol is dehydrated to sorbitan at 180°C using phosphoric acid as the catalyst. In the second stage, the sorbitan is esterified with the fatty acid at 220°C using sodium hydroxide as the catalyst. Sorbitan oleate has a hydrophilic (the sorbitol portion) area and hydrophobic (the fatty acid) portion. As a surfactant it is useful as an emulsifier and wetting agent in cosmetics and cleaners. Sorbitan oleate is another good dispersion agent, causing water soluble and water insoluble ingredients to combine in the product. It is used as a sweetening agent for foods, toothpaste and tobacco as well as in the manufacture of polyethers for polyurethanes and surfactants.

Chemical Structure: Sorbitan Oleate

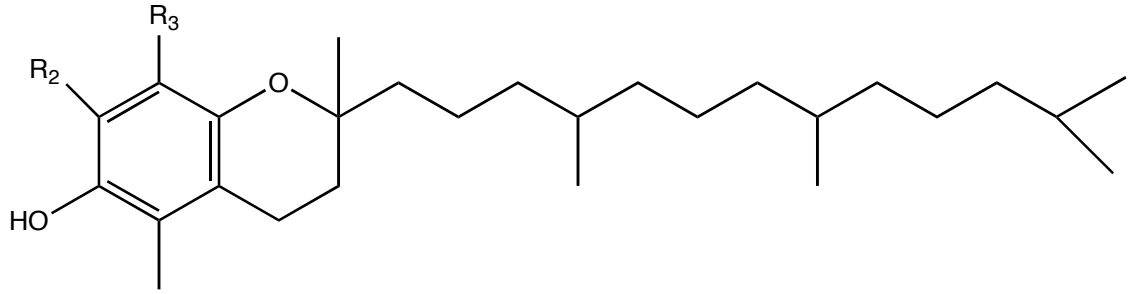


Tocopherol, which I recognized as a main chemical in Vitamin E, is present in one product, Nexxus Volumizing Foam Styler. I was very curious to find out what function it had in the product and after some research, found out that it is listed as tocopherol and not Vitamin E as to not mislead the consumer. Listing it as Vitamin E would give the impression that if offers a nutritional or health benefit such as an anti-oxidation or anti-cancer effect. In the case of this hair care product, it is present as an antioxidant to prevent chemical deterioration of the product.

Natural tocopherol exists as a mixture of four isomers, named alpha, beta, gamma and delta – tocopherol.

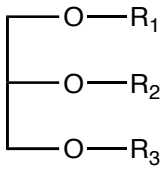
Isomer	**R_1**	**R_2**	**R_3**
Alpha-tocopherol	CH_3	CH_3	CH_3
Beta-tocopherol	CH_3	H	CH_3
Gamma-tocopherol	H	CH_3	CH_3
Delta-tocopherol	H	H	CH_3

Chemical Structure: Tocopherol

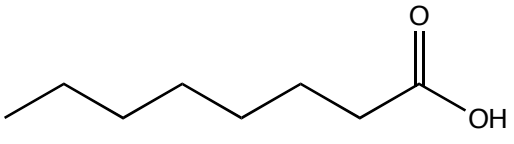


Caprylic/capric triglyceride is present in Bb Styling spray. It has excellent oxidation stability and helps make hair shiny and smooth. It is a triester lipid composed of glycerin, caprylic (octanoic acid) and capric (n-decanoic acid) fatty acids derived from coconut and palm kernel oils. With these longer nonpolar portions of the fatty acid chains, it is insoluble in water, soluble in warm alcohols, and miscible with fats and oils. It has a very low viscosity, is used as an emollient and lubricant, and is an excellent solvent for lipophilic active ingredients and UV filters. It is assumed that in this hair styling spray, it is acting as a solvent.

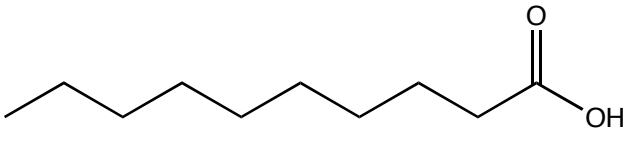
Chemical Structure: Caprylic/Capric Triglyceride



R1, R2, and R3 represent some mix of the fatty acids caprylic acid and capric acid



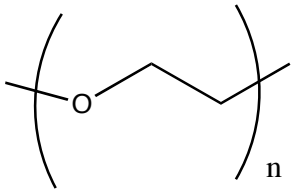
Caprylic acid



Capric acid

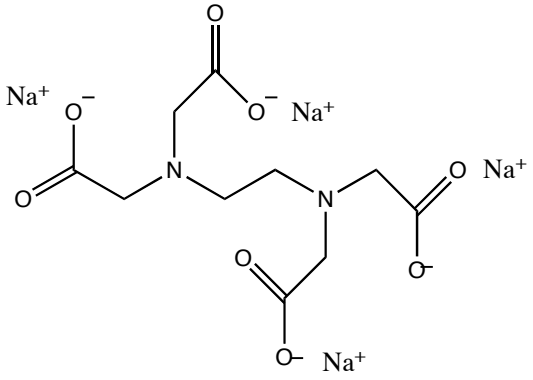
PEG stands for polyethylene glycol. Various forms of PEG compounds are mixed with fatty acids and fatty alcohols to create a variety of substances that have diverse functions in cosmetics, including surfactants, binding agents (to keep ingredients blended), stabilizers, and emollients. Pureology Pure Volume Blowdry Amplifier contains PEG-40 Hydrogenated Castor oil, and Nexxus Volumizing Foam Styler contains PEG-75.

Chemical Structure: PEG (Polyethylene glycol)

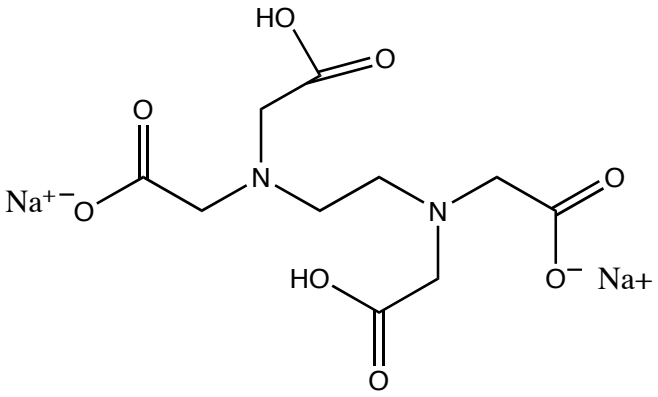


Tetrasodium EDTA is present in the Bb Styling Spray. EDTA is an abbreviation for ethylenediaminetetraacetic acid. EDTA is a chelating agent that combines with metal ions (minerals in water), in a one to one ratio regardless of the charge on the cation, forming stable, water-soluble complexes. The metal ion complexes with the O and N at several sites in the molecule, resulting in a structure that surrounds and isolates the cation. This process prevents unwanted changes in the product such as texture, odor (due to microbial growth) and consistency problems as a result of undesired reactions with metal ions.

Chemical Structure: Tetrasodium EDTA

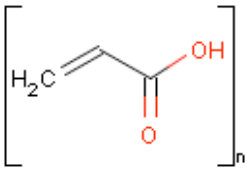


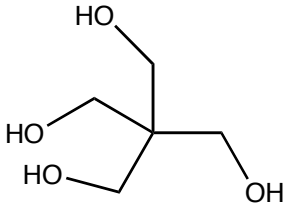
Chemical Structure: Disodium EDTA (ingredient of Sebastian Thickefy Styler)



Carbomer, an ingredient in Paul Mitchell Volumizing Spray, is a homopolymer (made from one type of monomer) of acrylic acid. It is crosslinked with an allyl ether of pentaerythritol, an allyl ether of sucrose, or an allyl ether of propanol. It serves as a thickening agent, acting as an emulsion stabilizer in the product and serves to adjust viscosity as well.

Chemical Structure: Carbomer (Polyacrylic acid)





Pentaerythritol

In summary, PVP/VA Copolymer, which forms elastic links between single hairs, is the only chemical substance common to all six hair thickening/volumizing products examined in this project. Four of the six products contain one or more types of quaternary ammonium salts, which serve to improve combability, prevent electrostatic charging of the hair and improve styling hold and elasticity of the hair. Several other different chemical substances in these products provide similar benefits. These substances include dimethicone copolyol and amodimethicone. Other chemical substances in the products act as surfactants, humectants, emulsifiers, preservatives, antioxidants, and solvents. Therefore, quite a number of chemical substances present in these products are not directly related to the specific function of thickening or increasing hair volume but rather serve more generic roles common to a variety of hair and cosmetic products. It must be noted, however, that specific

information for some of the chemical components (particularly polymers) could not be located, due to trade secret issues. I suspect that these specific substances contribute to the unique function of the product.

Thickeners and volumizers (outside of hair loss products) have gained significant popularity over the past 15 – 20 years, in step with the polymer industry. In addition, I suspect that their popularity has grown with consumer willingness, due to having more disposable income, to spend money on products designed to alter the texture of hair. When I was growing up, my mother, fashion conscious as she was, had hair spray as her only styling product. With six different thickening products sitting in my vanity, in addition to hair sprays, shampoos, and conditioners, I serve as evidence for this inference about today's consumer.

References – note: all electronic references were retrieved on the indicated date.

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Appendix I Hair Thickeners

Bb Thickening Spray

Water
Alcohol Denatured
Isopropyl alcohol
PVP/VA Copolymer
Polyquaternium-11
Hydrolyzed Wheat Protein
Hydroxypropyltrimonium Honey
PPG-12-PEB-65 Lanolin Oil
Quaternium-26
Hydroxyethyl Cetyldimonium Phosphate
Polysorbate 80
Fragrance

Bb Styling Spray

Water
Vinyl Caprolactam/PVP/Dimethylaminoethyl Methacrylate Copolymer
Diethylhexyl Malate
Caprylic/Capric Triglyceride
Myreth-3 Myristate
PVP/VA Copolymer
Glycerin
Amodimethicone
Cetrimonium Chloride
Tridecath-12
Acrylates/C10-30 Aklyl Acrylate Crosspolymer
Aminomethyl Propanol
Tetrasodium EDTA
Benzophenone-4
Phenoxyethanol
Methylparaben
Butylparaben
Ethylparaben
Propylparaben
Isobutylparaben
Fragrance

Sebastian Thickefy Styler

Water
VP/VA Copolymer
Cocamidopropyl Betaine
Panthenol
Ceteareth-20

Wheat Amino Acids
Cetrimonium Chloride
Polyquaternium-10
Polyquaternium-37
Amodimethicone
Tocopherol
Glycerin
PEG-75
Lanolin
PEB-12 Dimethicone
PPG-1 Trideceth-6
Laurtrimonium chloride
Fragrance
Phenoxyethanol
Benzyl Calicylate
Methylparaben
Hexyl Cinnamal
Propylene Glycol
Dicaprylate/dicaprate
Linalool
Propylparaben
Limoene
C10-12 Alkane/Cycloalkane
Benzyl Alcohol
Sorbitan oleate
Citric acid
Citral
Geraniol
Amyl Cinnamal
Citronellol
Cyclomethicone
Tredeceth-12
Potassium sorbate

Pureology PureVolume Blowdry Amplifier

Certified Botanicals of White Tea
Frankincense and Myrrh
PVP/VA Copolymer
Polyquaternium 11
Propylene Glycol
Methyl Gluceth-20
PEG-40 Hydrogenated Castor Oil
Panthenol
Quaternium 26
Polyquaternium 7
Polyquaternium 4

Dimethicone Copolyol
Hydroxyethyl cellulose
Citric Acid
Cinnamidopropyltrimonium Chloride (sunscreen)
Sunflower Seed Extract (Heliogenol) and Tocopheryl Acetate and Ascorbic Acid and Superoxide Dismutase and Melanin (Antioxidants)
Disodium EDTA
DMDM Hydantoin
Butylene Glycol
Methyl paraben
Aroma Therapy Fragrance

Paul Mitchell Volumizing Spray
Water
VP/VA Copolymer
Methacryloyl Ethyl Betaine/Acrylates Copolymer
PPG-5-Ceteth-20
Propylene Glycol
Bisamino PEG/PPG-41/3 Aminoethyl PG-Propyl Dimethicone/Hedychium Coronarium (White Ginger)/PEG-12 Dimethicone
Panthenol
Bisamino PEG/PPG-41/3 Aminoethyl PG-Propyl Dimethicone/Glutamine/yrosine/Leucine/Cysteine/Glycine/Symphytum Officinate/Plantago Major/Triticum Vulgare (Wheat) Protein/PEG-12 Dimethicone
Linoleamidopropyl PG-Dimonium Chloride Phosphate
Triethyl Citrate
Carbomer
Methylparaben
Diazolidinyl Urea
Propylparaben
Triethanolamine
Fragrance
Benzyl Salicylate Hydroxyisohexyl 3-Cyclohexene Carboxaldehyde
Butylphenyl Methylpropional
Linalool
Citronellol

Nexxus Volumizing Foam Styler
Water
PVP/VA Copolymer
Isobutane
Polyquaternium-4
Propane
Butane
Dimethicone Copolyol
Acetamide MEA

Polysorbate 80
Squalane
Diazolidinyl Urea
Fragrance
Hydrolyzed Collagen
Polyglyceryl-3 Distearate
Polysorbate 60
Myristic acid
Palmitic acid
Stearic acid
Guar Hydroxypropyltrimonium chloride
TriticumVulgare (Wheat) Bran Extract
Ceramide 3
Persea Gratissima (Avocado) Oil
Tetrahexyldecyl Ascorbate
Glycine Soja (Soybean) Sterol
Alpha-Glucan Oligosaccharide
Ethylhexyl Methoxycinnamate
Butyl Methoxydibenzolmethane
Tocopheryl Acetate