

Citrate Polyesters

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Over the last decade, our industry has undergone a dramatic metamorphosis. This change has been a result of consumer demand, government regulation and a realization that we are stewards of our environment.

The introduction of new materials for use in the personal care market has been complicated by several factors. The successful products will be;

- (1) based upon sustainable raw materials;
- (2) polymers (meeting the requirements of REACH);
- (3) free of vinyl monomers which are considered toxic (that is; made from raw materials that are friendly both to the consumer and the environment);
- (4) offering the formulator advantages that cannot be found in other materials meeting the other three requirements.

SurfaTech Corporation has introduced a series of Citrate Esters that meet all of the requirements listed above.

Sustainable Raw Materials

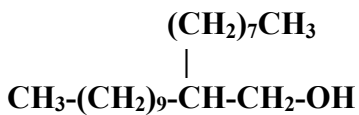
The raw materials used for the preparation of the citrate esters are derived from natural raw materials.

Stearyl Alcohol

Stearyl alcohol is $\text{CH}_3(\text{CH}_2)_{17}\text{-OH}$. It is derived from coconuts.

Octyldodecanol

Octyldodecanol is:



It is derived from coconuts.

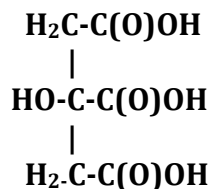
1, 3 Propanediol



Zemea[®] propanediol is a colorless and highly purified glycol derived from a sustainable and renewable corn sugar fermentation process. Approved by Ecocert™ and certified by the Natural Products Association (NPA), Zemea[®] is a 100% natural ingredient. Zemea[®] propanediol is the perfect glycol compound for formulations where non-petroleum based ingredients are desired. The benefits of Zemea[®] propanediol include purity, lack of irritation and sensitization, and environmental sustainability

Citric Acid

Citric acid is: (I lined up the structure)



Citric acid is a product of the fermentation of glucose.

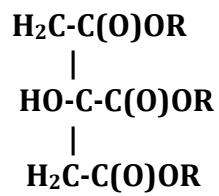


Molecular design

The first class of materials is the triester. For example Tri-octyldeceyl citrate is a known material.

Molecules with no reactive carboxyl groups

Tri-substituted citrate esters



R is a mixture of

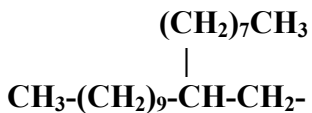
50% $-(\text{CH}_2)_{17}-\text{CH}_3$

and

50% $\begin{array}{c} (\text{CH}_2)_7\text{CH}_3 \\ | \\ \text{CH}_3-(\text{CH}_2)_9-\text{CH}-\text{CH}_2- \end{array}$

The product is a slushy liquid.

When R is:



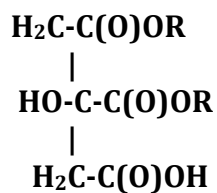
This product is tri-octyldodecyl citrate¹; a liquid C66 ester. It is not a polymer under REACH. And since all three acid groups are esterified it cannot be incorporated into a polymer. (Although some may argue that the OH could be reacted into a polymer; but with difficulty)

Polymers

High Definition Polymers[®] are the product of molecular modeling, allowing the chemist to focus in on every detail of the molecule in order to dial in the desired aesthetics .. Three different types of alcohols are incorporated in order to provide different properties to these products. The liquid C₂₀ octyldodecanol is a highly branched molecule that stays liquid and provides cushion. This material helps spread the product on the skin and while it does have cushion it leaves a very light dry feel on the skin. Use of a solid C₁₈ stearyl alcohol leaves a soft barrier on the skin and provides structure. This product has a melting point close to body temperature allowing it to liquefy when applied to the skin.

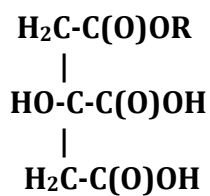
Chain Terminators

Chain terminators have one group that is reactive. For simplicity, we are showing the carboxyl group on the third carbon as the reactive species, but from an esterification point of view would be equally reactive on each of the three positions..



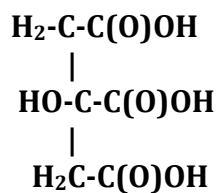
Chain Extenders

Chain extenders have two groups that are reactive. For simplicity, we are showing the second and third carbon as the reactive ones, but from an esterification point of view all three are equally reactive.



Chain Branching

Chain branching groups have all three groups available for reaction.



Crosslinking Groups

The reactive carboxyl groups are linked to each other using a 1,3 propanediol derived from corn.

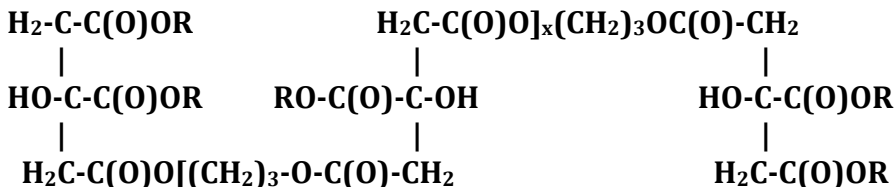


It is only when all of these materials are combined in the proper ratio that the desired products are obtained. The reaction forms a polyester, and includes no vinyl reactive groups. Also there are no undesirable monomers.

When the components which are crosslinked are simply combined with each other as individual components in the same ratio as that used to make a polymer, the mixture is a non-uniform mixture of all components. Photomicrographs clearly show this.

When reacted the same ratio of components are then crosslinked with 1,3 propanediol a polymer is formed that no longer is simply a mixture, but is a condensation polymer having a very specific structure and consequently a very specific properties.

The most simple representation of the polymers is one in which all the reactive positions are as shown.



Chain Terminator (Chain Extender)_x Chain Terminator

Photomicrographs

The photomicrographs and conclusions provided in this section were provided by

Microtrace LLC
790 Fletcher Drive
Suite 106
Elgin, IL 60123-4755

•The following samples were submitted for photomicrographic evaluation:

- 1. **Non-crosslinked** - citrate ester with no crosslinking having 50% by weight C₁₈ (stearyl) and 50% C₂₀ branched (octyldodecanol).

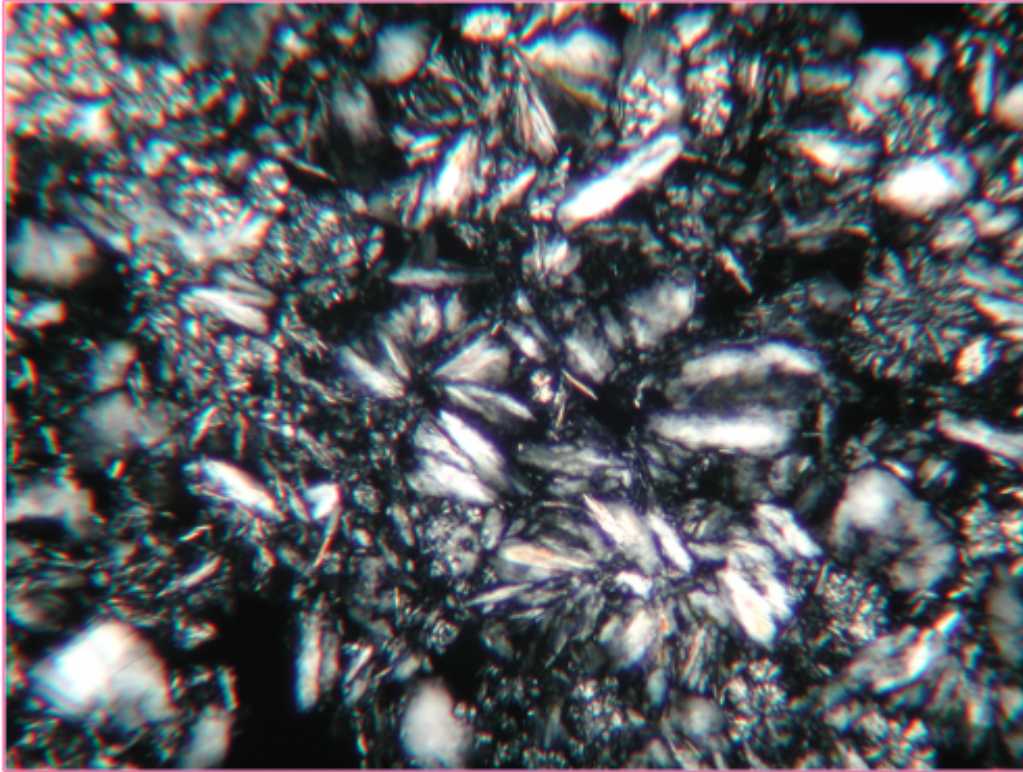
and

- 2. **Crosslinked** citrate ester having 50% by weight C₁₈ (stearyl) and 50% C₂₀ branched (octyldodecanol), crosslinked with 1,3 propane diol.

Non-crosslinked Photomicrographs

All four components are clearly seen. The large crystals (laths and blocky crystals) melt between approximately 39°C and 42°C. The fine acicular crystals begin to melt at approximately 44°C and all of these crystals have melted by 55.8°C with most having melted by 50°C. The black areas are the liquid phase.

Photomicrograph A



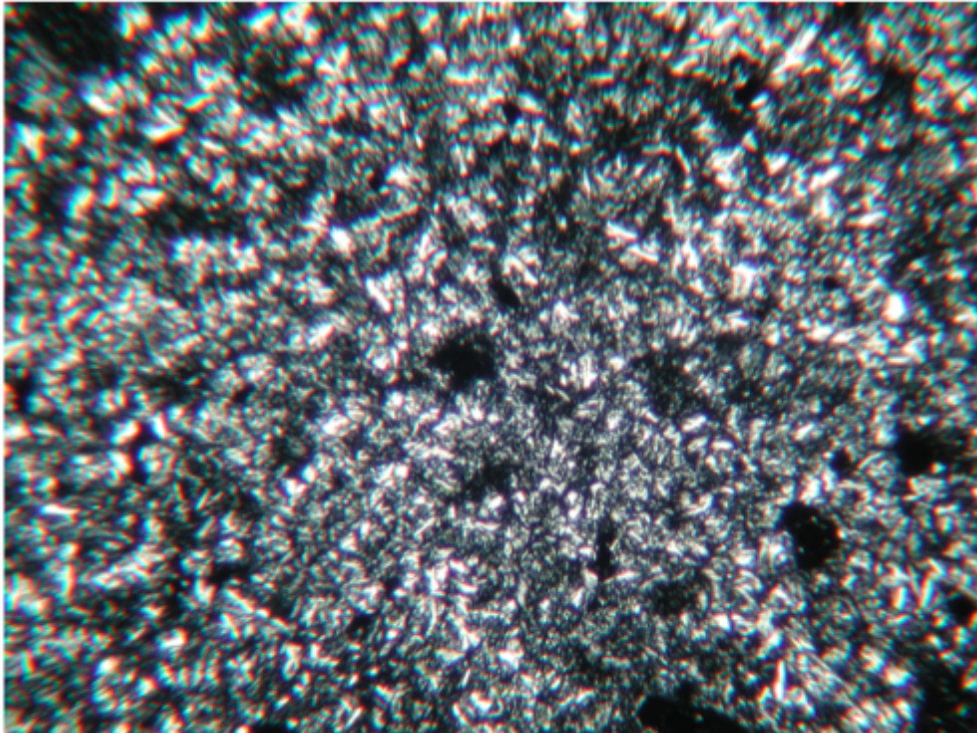
- The non-crosslinked material is a viscous liquid containing three types of anisotropic crystals suspended in an isotropic liquid phase. The crystals have a bimodal particle size distribution.
- The large blocky crystals melt over the range of 39° - 42.2°C
- The small needle-like crystals melt over the range of 44° - 55.8°C. Melting is appreciably complete by ~50°C with only a few crystals melting at 55.8°C. The crystals disappear into the liquid phase as they melt.
- The onset of melting is approximate since it is difficult to see individual crystals melting when there are many of them in the field.

Polymer

The introduction of crosslinking makes the product a polymer, rather than a collection of non-polymeric materials.

The product consists of uniformly sized acicular to narrow lath shaped crystals. Melting of the crystals occurs over a wide temperature range. The onset of melting is difficult to recognize (approximately 42°C) and approximately one half of the crystals have melted by 45°C. The last of the crystals melts by 48.4°C. Black regions are the liquid crystal phase.

Photomicrograph B



- The crosslinked product is a thick paste consisting of a single anisotropic crystalline phase.
- The crystalline phase melts over the range of ~ 42°C to 48.4°C. By ~ 45°C most of the crystals have melted and disappeared into the liquid phase.
- The crystals exhibit a narrow particle size distribution and are significantly smaller in size than the large crystals (lower melting phase) in the non-crosslinked product.

Commercial Crosslinked Polymer Products

Product	INCI	Description
CosmoSurf [®] CE-100	octyldodecyl citrate Crosspolymer	Liquid lower viscosity (ECOCERT Approved)
CosmoSurf [®] CE-100HV	octyldodecyl citrate crosspolymer	High molecular weight liquid (ECOCERT pending)
CosmoSurf [®] CE-140	octyldodecyl stearyl citrate crosspolymer	Soft wax (ECOCERT pending)
CosmoSurf [®] CE-150	octyldodecyl stearyl citrate crosspolymer	Medium hardness wax (ECOCERT pending)
CosmoSurf [®] CE-250	octyldodecyl behenyl citrate crosspolymer	Hard Wax (ECOCERT pending)

Water Proofing Study

Lott Research, Inc undertook a study to determine if Cosmosurf CE-150 (SurfaTech Corporation) could be used as a waterproofing film former for sunscreen products.

Method

Formulas were prepared as shown:

Ingredient	LRI A80	LRI 220	LRI A175
	%	%	%
Part A			
Water	74.2	72.2	82.9
Carbomer	.25	.25	.25
Disodium Ethylenediaminetetraacetic Acid	.05	.05	.05
Triethanolamine	1	1	1
Part B			
Octocrylene	3	3	3
Octisalate	3	3	3
Oxybenzone	2	2	2
Avobenzone	1	1	1
Stearic Acid	2	1	1
Sorbitan Isostearate	0	1	1
Polyglyceryl-3 Distearate	0	1	1
Glyceryl Stearate Self Emulsifying	3	0	0
Benzyl Alcohol	1	1	1
Dimethylpolysiloxane	.5	.5	.5
VP/Eicosene Copolymer	0	0	2
Methylparaben	0	.2	.2
Propylparaben	0	.1	.1
Finsolv TN	8	0	0
Cosmosurf CE-100	0	2	0
Part C			
Liquipar PE(Phenoxyethanol, Isopropylparaben, Isobutylparaben, and n-Butylparaben	1	0	0

The manufacturing procedure was basically the same for all three products; Part A and B were heated separately to about 160(put in degree signs)F, B added to A while

rapidly stirring, cooled with stirring to approximately 105 F and Part C was added with stirring.

All three formulas were SPF tested using a single port Solar Light Model 15S Xenon Arc, Solar Simulator lamp, which has a continuous light spectrum in the UVA and UVB range (290-400 nanometers). The spectral output of the solar simulator is filtered so that it meets the spectral output requirements for testing Sunscreen Drug Products for over-the-counter human use; Proposed Amendment of Final Monograph, CFR Part 352.70 (b) Light Sources, Federal Register, Vol. 72, No. 165, Aug. 27, 2007 and the International Sun Protection Factor (SPF) Test Method, May 2006.

The SPF test for all three formulas was performed on the same subjects. The only difference was that LRIA80 was performed as a static, non water resistant test and LRI A220 and LRI A175 were performed as an 80 minutes VWR test.

All three formulations were submitted to an independent analytical lab, Allied Analytical Laboratory Services.

Results

The average values for the SPF tests as reported by Florida Suncare Testing, Inc. were as follows:

LRI A80	≤ 19(static)	No waterproofing Agent
LRI 220	28.85(VWR)	VP/Eicosene Copolymer
LRI A175	29.05(VWR)	Cosmosurf CE-150

The analytical results for the formulations are shown below in % by weight.

	Octocrylene	Octisalate	Oxybenzone	Avobenzone
LRI A80	3.03	3.12	2.02	1.04
LRI A220	2.94	3.04	1.95	0.95
LRI A175	3.04	2.96	1.99	1.00

Discussion

All three formulas were targeted as an SPF 25. For an SPF 25 the lowest number obtainable is a SPF19. Four of the subjects had MED responses at the SPF 19 level. When this happens it means the actual value is at a maximum SPF 19. Based on discussions with the Florida Suncare Testing, Inc. investigator the values would probably have been considerably lower than 19. The investigator estimated that the actual value would probably have been closer to SPF 12- 15 based on the responses at SPF 19. For a 5 subject study, the values obtained for LRI A220 and LRI A175, with standard deviations of 2.53 and 4.12 respectively are not statistically different.

Conclusion

Based on the results of these SPF tests has significant value as a SPF waterproofing agent when compared to a control formula without a waterproofing film former. Based on the results of this study, SurfaTech Cosmosurf CE-150 was equivalent to the well-known waterproofing film former, VP/Eicosene Copolymer.

SPF Improvement

Formula A

Ingredient	Item Code	Percent
Part A		
	Water	67.2000
	Ultrez 21	0.2500
	EDTA	0.0500
Part B		
	TEA	1.0000
Part C		
	Octocrylene	3.0000
	Octisalate	3.0000
	Oxybenzone	2.0000
	Avobenzone	1.0000
	Stearic Acid	2.0000
	GMS SE	3.0000
	Siltech F200	1.0000
	DC 200-200	0.5000
	Finnsolv TN	8.0000
	Spider Ester®ESO	5.0000
	Cosmosurf®CE-100	2.0000
Part D		
	Lipuipar PE	1.0000
Total		100.00

SPF 31.55 (5 subjects)

SPF tested using a single port Solar Light Model 15S Xenon Arc, Solar Simulator lamp, which has a continuous light spectrum in the UVA and UVB range (290-400 nanometers). The spectral output of the solar simulator is filtered so that it meets the spectral output requirements for testing Sunscreen Drug Products for over-the-counter human use; Proposed Amendment of Final Monograph, CFR Part 352.70 (b) Light Sources, Federal Register, Vol. 72, No. 165, Aug. 27, 2007 and the International Sun Protection Factor (SPF) Test Method, May 2006.

Spider Ester and Cosmosurf are registered trademarks of SurfaTech Corporation. Spider Esters are the topic of several patents²⁻⁵

Formula B

Ingredient	Item Code	Percent
Part A		
	Water	67.2000
	Ultrez 21	0.2500
	EDTA	0.0500
Part B		
	TEA	1.0000
Part C		
	Octocrylene	3.0000
	Octisalate	3.0000
	Oxybenzone	2.0000
	Avobenzene	1.0000
	Stearic Acid	2.0000
	GMS SE	3.0000
	Benzyl Alcohol	1.0000
	Siltech F-200	0.5000
	Finsolv TN	15.0000
Part D		
	Lipuipar PE	1.0000
Total		100.00

SPF 18.87 (5 subjects)

SPF tested using a single port Solar Light Model 15S Xenon Arc, Solar Simulator lamp, which has a continuous light spectrum in the UVA and UVB range (290-400 nanometers). The spectral output of the solar simulator is filtered so that it meets the spectral output requirements for testing Sunscreen Drug Products for over-the-counter human use; Proposed Amendment of Final Monograph, CFR Part 352.70 (b) Light Sources, Federal Register, Vol. 72, No. 165, Aug. 27, 2007 and the International Sun Protection Factor (SPF) Test Method, May 2006.

Shampoos

CosmoSurf CE-100 together with Silplex J-2S (What is this?) has been found to be an effective agent for the formation of a coacervate in shampoos.

Shampoo Formulation			
2 in 1 Shampoo (Coacervate) FH183D			
Part ID	Description)	INCI Name	weight %
A			
	D.I. Water	Aqua	22.000
	Carbopol Aqua SF-1 Polymer (1%)	Acrylates copolymer	2.500
	TEA 99%	Triethanolamine	0.200
	Na ₂ EDTA	Disodium EDTA	0.100
	Sodium Laureth Sulfate	Sodium Laureth-2 Sulfate	27.500
	Cocamidopropyl Betaine	Cocamidopropyl Betaine	6.000
B			
	D.I. Water	Aqua	18.000
	Sodium Laureth Sulfate	Sodium Laureth-2 Sulfate	5.500
	Cocamidopropyl Betaine	Cocamidopropyl Betaine	4.000
	Ninol COMF	Cocamide MEA	1.200
	EGDS	Ethylene Glycol Distearate	3.000
C			
	Silplex J2-S (Siltech LLC)	Silicone Quaternium-20	1.000
	Cosmosurf® CE-100 (SurfaTech)	Octyldodecyl citrate crosspolymer	1.000
	Wheat Protein	Wheat Protein	0.500
	Hemp Seed Oil	Cannabis Sativa (Hemp) Seed Oil	1.000
	Nipaguard DMDMH	DMDM Hydantoin	0.500
D			
	Decyl Glucoside	Decyl Glucoside	3.000
	Amphosol 2C	Disodium Cocoamphodiacetate	3.000
	Citric Acid (40% aq)	Citric Acid	q.s.
	Sodium Chloride (if needed)	Sodium Chloride	q.s.
	Crothix (Croda) (if needed)	PEG-150 Pentaerythrityl Tetrastearate	q.s.
	Fruity Herbal	Fragrance	q.s.
		Total	100.000

- Procedure:**
1. Into a clean and sanitized stainless steel container equipped with propeller mixer, add water in Phase B
 2. Add SLES-2 and Betaine, heat up to 70 to 75 C, slowly add Cocamide MEA and EGDS, mix slowly while minimizing air incorporation. Mix until uniform, then cool down to room temperature.
 3. In another clean and sanitized stainless steel tank equipped with propeller mixer, add water and the rest of ingredients of phase A one by one while minimizing air incorporation. Mix until uniform.
 4. Add phase B slowly into Phase A. Mix until uniform
 5. Premix Silplex J2-S and Cosmosurf CE-100 until uniform, then add into Phase A+B, mix well. Add the rest of ingredients in Phase C one by one into Phase A+B until homogeneous while minimizing air incorporation.
 6. Add ingredients in Phase D one by one. Adjust pH by using citric acid to pH = 5.5 ~ 6.5, and adjust viscosity to 6,000 cps ~ 12, 000 cps by adding q.s. NaCl and Crothix. Add fragrance if necessary.

Properties

Viscosity (cps)	12,000
pH	5.70
Appearance	Opaque white cream

FOAM

Method: All products were evaluated with the same procedure. A 1000 mL cylinder with 10 mL increments was used. All samples and distilled water were prepared at 25 °C. 1.00 gram of test material was used and 100 ml distill water was added to dissolve the test material in a 250 ml beaker. After the test material was totally dissolved, the solution was transferred into the cylinder. An outlet of air pump was sited on the bottom of the cylinder to generate the bubbles. Record the foam height within 20 seconds for each test materials, each material was evaluated 3 times and their averages were documented.

The scale for Foam Height is 1000 ml is considered outstanding and 100 mL is very poor. The type of foam was also noted whether it is tight or loose. Bubbles were generated by electronic air pump.

<i>Sample (Bubble for 20 sec)</i>	<i>Initial Reading (Average, ml)</i>	<i>Two Minute Reading (average, ml)</i>	<i>Five Minute Reading (average, mL)</i>
FH183D	700	690	670

Foam was tight and uniform.

Wet Comb

All products were evaluated on 10-inch Virgin Brown Hair.(Need to identify source of 10 inch virgins...just kidding) Two x 2-gram swatches were used for each material tested, all from the same lot. All swatches were wet with 25 °C water and one gram of test material was used for each swatch. Swatches were washed and then rinsed for at least one minute per swatch. Wet Comb Evaluation was then performed. No blow-drying of hair was done. All swatches air-dried then the Dry Comb Evaluation was performed once hair was completely dry.

Scale used is 1 to 5, 5 being the best. Used for wet and dry combing.

Evaluation Sample	Wet Comb	Rinse off	Clean Feel (Scroop)	Shine	Residual Feel	Average
Control Water only	1.0	3.0	2.0	2.0	2.0	2.0
FH183D	4.5	4.5	4.5	3.0	3.0	3.9

Dry Comb

Evaluation Sample	Dry Comb	Dry Feel	Clean Feel /Look	Shine	Fullness /Manageable	Fly-away	Residual Feel	Static	Average
Control Water only	3.0	3.0	2.0	1.0	1.0	1.0	1.0	2.0	1.75
FH183D	4.4	4.5	4.0	4.0	4.4	4.2	3.5	4.0	4.12

Salt Tolerance, pH, Viscosity, Ease of Formulation, Effect on Formulation Stability:

Scale used is 1 to 5, 5 being the best, only for salt tolerance, Ease of formulation, effect on formulation stability. Viscosity was tested by using Brookfield, LVT, #4 spindle, 12 rpm.

Evaluation Formula	Salt Tolerance	pH	Viscosity, cps	Ease of Formulation	Effect on formulation Stability	Average
FH183D	2.5	5.70	12,000	4.0	4.5	3.67

Antiperspirant with Cosmosurf CE-100 and Silwax CR-1

<u>Phase</u>	<u>Ingredient</u>	<u>INCI Name</u>	<u>A</u> <u>%w/w</u>
Part A	Reach AZP-908 (Summit Research)	Aluminum/Zirconium Tetrachlorohydrate-GLY	24.00
	Silsurf DMC-AP (Siltech)	PEG/PPG 18/6 Dimethicone	2.50
Part B	Silwax CR-1 (Siltech)		25.00
	Cosmosurf CE 100		5.00
Part C	Fancol IH-CG (Fanning)	Isohexadecane	9.00
	Probutyl 14 (Croda)	PPG-14 Butyl Ether	9.00
	Castorwax NF (Vertellus)	Hydrogenated Castor Oil	2.50
	Protomate 400-DS (Protameen)	PEG-8 Distearate	1.00
	Crodacol S-95 NF (Croda)	Stearyl Alcohol	18.00
Part D	270764 Talc USP 300 BC 127 (Brenntag)	Talc	3.00
	Cab-O-Sil M-5 (Cabot)	Silica	0.50
Part E	Fragrance Blue Musk (Lebermuth)	Fragrance (Parfum)	<u>0.50</u>
			<u>100.00</u>

Procedure:

1. In a side vessel, combine Phase A ingredients. Impeller mix to uniformity.
2. In main vessel, heat Phase B ingredients to 70°C under agitation. Continue mixing and add Phase A. Bring to 75°C.
3. Combine Phase C in side vessel, heat to 85°C under impeller agitation and mix to uniformity.
4. Add Phase C to AB under homogenization. Maintain batch at 80°C.
5. Pre-combine Phase D. Add to batch under homogenization. Begin cooling.
6. Add Phase E at 70°C under homogenization. Continue cooling.
7. Pour batch into sticks at 65°C.
8. Heat-treat surfaces.

Reference

1. U.S. Patent 4,868,236 to O'Lenick et al issued September 19, 1989.
2. U.S. Patent 7,723,456 to O'Lenick et al issued May 25, 2010.
3. U.S. Patent 7,569,607 to O'Lenick et al issued August 4, 2009.
4. U.S. Patent 7,473,707 to O'Lenick et al issued January 6, 2009.
5. U.S. Patent 7,462,729 to O'Lenick et al issued December 9, 2008.