



Guerbet Citrate Esters

These esters give nonirritating, high-cushion emolliency; fluoro-guerbet citrates provide breathable, nonocclusive films

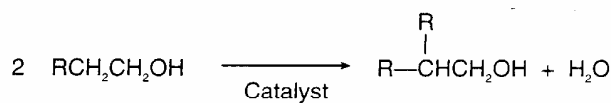
Anthony J. O'Lenick, Jr.
Jeffrey K. Parkinson
Siltech Inc., Norcross, GA, US

Charles W. Buffa
Biosil Technologies Inc., Englewood, NJ, US

Guerbet alcohols are key raw materials used in the preparation of citrate esters and fluoro-citrate esters for personal-care applications. Many of the esters' functional attributes are a direct result of the guerbet alcohol chosen. Since guerbet alcohols are not universally understood, we will first review the chemistry of these important raw materials.

Background

Marcel Guerbet¹ first synthesized these materials in the 1890s. The reaction sequence that bears his name is related to the aldol condensation reaction. It requires high temperatures and a suitable catalyst (Equation 1). An alcohol with twice the molecular weight of the reactant alcohol minus a mole of water results.



Equation 1. Synthesis of Guerbet alcohols (R is alkyl)

Properties: Guerbet alcohols have a high molecular weight, hence:

- They have low irritation properties. Because of their high molecular weight, they do not penetrate the skin to cause irritation.
- They are branched. Therefore, they are liquid to extremely low temperatures (Figure 1).
- They have low volatility.
- They are primary alcohols. Because of their resultant reactivity, they can be used to make many derivatives.
- They are useful as superfatting agents to re-oil the

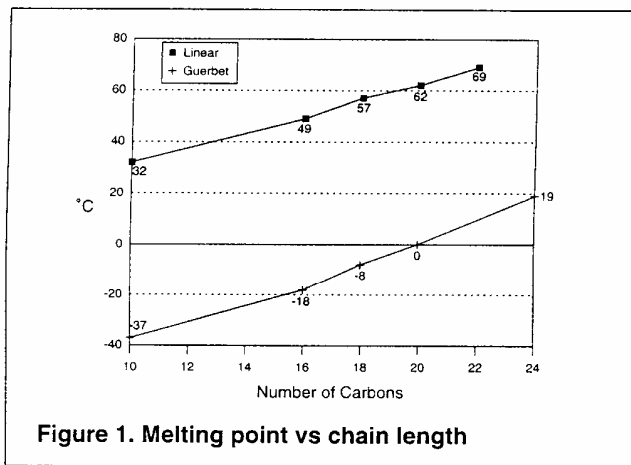


Figure 1. Melting point vs chain length

skin and hair.

- They are good lubricants.

Guerbet alcohols are essentially saturated. Because of this, they exhibit very good oxidative stability at elevated temperatures. They also have excellent Gardner colors initially and even when stored at elevated temperatures. They exhibit better stability than do unsaturated alcohols in many formulations.

Of the several manufacturers of guerbet alcohols, some use oxo alcohols and some use natural alcohols as raw materials. Guerbet alcohols are useful in personal care and many other applications,^{2-5,7-13} but they also make outstanding raw materials for a variety of derivatives useful to personal-care formulators. For details on guerbet alcohol chemistry and surfactant derivatives, see Reference 14. We will limit this discussion to two specific, patented classes of guerbet esters, the citrate and fluoro-citrate esters of guerbet alcohols.

Reproduction in English or any other language of all or part of this article is strictly prohibited.

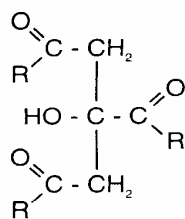


Figure 2. Tri(octyl dodecyl) citrate; R, the octyl dodecyl moiety, is derived from the guerbet alcohol.

Table 1. Solubility of various esters (5% Product w/w)

Material	Octyl dodecyl dodecyl citrate*	Octyl dodecyl stearate	Hexyl laurate
Safflower oil	soluble	soluble	soluble
Castor oil	soluble	soluble	soluble
Mineral oil	soluble	soluble	soluble
Octyl palmitate	soluble	soluble	soluble
Oleyl alcohol	soluble	soluble	soluble
Water	insoluble	insoluble	insoluble
Propylene glycol	insoluble	insoluble	insoluble
Ethyl alcohol	insoluble	insoluble	insoluble
Property			
Molecular Weight	1065	573	284
Cushion	High	Middle	Low

* Patented product of Siltech Inc. Norcross, GA

Formula 1. Blooming bath product

A. Glyceryl stearate	5.00%
Cetareth-12	5.00
CE-2000 1&a+.3R	15.00
Coco caprate	15.00
B. Water	58.00
Propylene glycol	2.00

Procedure: Into an appropriate kettle, add A in order shown. Heat to 70°C. Into another kettle, add B in order shown; heat to 70°C. Add B to A under agitation. Cool under agitation. Notes: The triguerbet citrate is an emollient.

Formula 2. Micro titanium dioxide sunscreen lotion

A. Water	62.80%
B. Propylene glycol	4.00
Methylparaben	0.20
Propylparaben	0.30
C. Micro titanium dioxide	5.00
Octyl palmitate	7.00
PF2	1.00
Emulsifying wax NF	2.00
Stearic acid	3.00
Hydroxyethyl cellulose	0.50
D. Triethanolamine	0.70
Water	2.00
E. Water	1.00
Imidazolidinyl urea	0.50
Fragrance	0.20

Procedure: Into an appropriate kettle, add B in order shown. Heat A to 70°C. Add B to A at 70°C. Add C in order shown under good agitation, keeping the temperature at 70 to 75°C. After the mixture is homogeneous add D under sweep agitation. Cool to 45°C under sweep agitation and add E in order shown.

Sources

1. Lipo Chemical, Paterson, NJ
2. Siltech Inc., Norcross, GA

Formula 3. Cleansing cream

A. Glyceryl stearate	6.00%
Stearic acid	4.00
Petrolatum	10.00
Mineral oil	10.00
Isopropyl myristate	10.00
CE-2000	2.00
B. Water	50.00
Propylene glycol	6.00
Triethanolamine, 99%	1.00
C. Vitamin E	1.00

Procedure: Into an appropriate kettle, add A in order shown. Heat A to 70°C. Into another appropriate kettle, add B in order shown and heat to 70°C. Add B to A under agitation. Allow to cool and continue to mix. Add C at 50°C. Emulsion will invert at about 37°C. Continue agitation until temperature reaches 30°C.

Sources

1. Siltech Inc., Norcross, GA

Guerbet Citrate Ester Chemistry

Reacting equimolar quantities of guerbet alcohol and citric acid at elevated temperatures (180-195°C) in the presence of an esterification catalyst and distilling off the resulting water gives a series of esters conforming to the structure shown in Figure 2.^{14a}

Properties: These esters are high-viscosity oils with light color and low odor. They can help formulators prepare pressed powders or disperse pigments. Two pigments of particular interest are titanium dioxide and zinc oxide, both used in sun-care products.

The high molecular weight of the guerbet citrate esters helps them provide good cushion as emollients. For example, octyl dodecyl citrate is a 66-carbon liquid triester. Its chemical properties and solubilities in a variety of materials are provided in Table I.

The liquidity of an ester with a molecular weight this high is surprising. It results from the guerbet branching in the molecule. For comparison, we include the most liquid of common personal-care esters.

Octyl dodecyl citrate, added as the oil phase or a component of the oil phase, provides cushion, refatting properties and emolliency (Formulas 1-3).

Fluorinated Esters

More recently, fluorine has been incorporated into the guerbet citrate to produce a series of patented esters.^{15,b} The reaction involves replacing one-third equivalent of the total alcohol with a fluoro alcohol. It is important to note that the product is a perfluoroethylene. The two methylene groups present between the fluoro groups and the oxygen make the product a perfluoroethylene alcohol. The ethylene linkage adds product stability.¹⁶

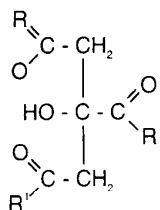
The fluoro-guerbet citrate esters conform to the generic structure shown in Figure 3.

Properties: Including fluorine in the citrate ester results in several desirable properties. To show this, a non-fluorinated tri-guerbet citrate^c was compared to di-

^apatented and marketed by Siltech

^bmarketed by Biosil Technologies

^cSiltech CE-2000, Siltech



R is derived from a guerbet alcohol.
 R' is derived from a fluoro alcohol conforming to the following structure:

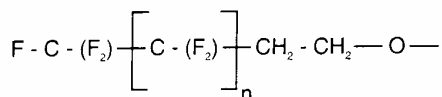


Figure 3.

(octyldodecyl)-fluoro-heptyl-citrate.¹

Formulas 4-8 use the fluoro-guerbet ester for its ability to provide a breathable thin film that also shows barrier properties. There is little cushion to these products in many applications, where barrier properties and thin non-occlusive films are wanted. In others, oily films with cushion are desired. Here, the inclusion of fluorine in the molecule improves the ester's spreadability on the skin.

¹Biosil Basics Fluoro Guerbet 3.5. Biosil Technologies

Formula 4. Spray-on leave-in conditioner

A. Water	97.10%
B. Quaternium 15	0.15
C. Silamine C-100	1.50
D. Fluoro Cyclic Guerbet 3.5	1.00
E. SPQ	0.25

Procedure: Into an appropriate kettle, add A and B. Mix well. Add C, D and E in order shown under agitation. Notes: The dimethicone copolyol amine provides softening and improves combability. Fluoro Cyclic Guerbet 3.5 provides gloss to hair.

Sources

1. Biosil Technologies Inc., Englewood, NJ
2. Siltech Inc., Norcross, GA

The evaluation indicated that guerbet esters containing fluorine show several significant, unexpected differences from the non-fluoro products:

- The fluorine products form a breathable, nonocclusive barrier.
- They also form thinner films on the skin for a more comfortable feel.
- The cushion observed with the non-fluorinated materials is not seen with the fluoro materials.
- Skin-care products incorporating the fluoro-guerbet products gain increased slip and improved lubrication and emolliency.
- Introduction of fluorine into the molecule helps set

Formula 5. Body countouring cream

A. Water	59.50%
Propylene glycol	3.00
B. Emulsifying wax NF	8.00
Cetyl alcohol	2.00
Glyceryl stearate	2.00
Capric/caprylic triglyceride	4.00
Rice bran oil	5.00
Biosil Basic Fluoro Guerbet 3.5	2.00
C. F-350	1.00
D. Undebezofene	1.00
E. <i>Aloe vera</i> extract	1.00
<i>Ascophyllum</i> extract	1.00
Ivy extract	1.00
<i>Centella asiatica</i> extract	1.00
F. Theophyllisilane C	4.00
Algisium C	3.00
Menthol	0.50

Procedure: Into an appropriate kettle, add A; heat to 70°C. Into another appropriate kettle, add B; heat to 70°C. Add A to B under agitation. Cool to 50°C and add C slowly under agitation. Add D under agitation once the temperature has cooled to 45°C. Add E in order shown, under agitation, once temperature has reached 30°C.

Sources

1. Biosil Technologies Inc., Englewood, NJ
 2. Siltech Inc., Norcross, GA
- Biosil Basics Fluoro Guerbet 3.5 provides thin non-occlusive film with good spreadability.

Formula 6. Body Contouring Cream, Time-Release

A. Water	39.90%
Propylene glycol	3.00
B. Emulsifying Wax NF	8.00
Cetyl Alcohol	2.00
Glyceryl Stearate	2.00
Capric Caprylic triglyceride	4.00
Rice Bran Oil	5.00
Biosil Basic Fluoro Guerbet 3.5	2.00
C. F-3502	1.00
D. Undebezofene	1.00
E. Herbal Slimming Complex 17-EB-1	5.00
Nanospheres 100 Theophyllisilane C	4.00
Nanospheres 100 Algisium C	3.00
Zedomine	0.10

Procedure: Into an appropriate kettle, add A; heat to 70°C. Into another appropriate kettle, add B; heat to 70°C. Add A to B under agitation. Cool to 50°C and add C slowly under agitation. Add D under agitation once the temperature has cooled to 45°C. Add E in order shown under agitation once temperature has reached 30°C.

Sources

1. Biosil Technologies Inc., Englewood, NJ
 2. Siltech Inc., Norcross, GA
- Biosil Basics Fluoro Guerbet 3.5 provides thin non-occlusive film with good spreadability.

the color in eyeshadow and lipstick.

Conclusions

Many of the functional properties of guerbet alcohol citrate esters derive from the parent guerbet alcohol. These include both liquidity at low temperatures and stability. The non-fluorinated ester is an oil product that has cushion and emolliency. Adding fluorine to the molecule decreases cushion but increases spreadability on the skin and hair and provides barrier properties and gloss to the hair and skin.

References

Address correspondence to Anthony O'Lenick, Jr. c/o Editor, *Cosmetics & Toiletries* magazine, 362 South Schmale Road, Carol Stream, IL 70188-2787 US.

1. M Guerbet, *C.R. Acad. Sci. Paris*, 128, 511; 1002 (1899)
2. AA Kassem and SA Said, Lipsticks, cleansing milks and foundation emulsions, *Cosm Perf* **90** (1) 31-35 (1975)
3. AA Kassem and SA Said, Performance of dialkyl sulphate-lauric monoethanolamide-PVP/VA shampoo in the presence of superfatting materials, *Cosm Perf* **88** (8) 35-38 (1973)
4. HM Lee and M Coopersmith, Effect of cosmetic oils on aerosol antiperspirant formulations, *Cosm Perf* **88** (5) 35-38 (1973)
5. Lipsticks, resin based, *Japan* **70** 41 (12) 318 (1970)
6. AJ O'Lenick and RE Bilbo, Guerbet alcohols, a versatile hydrophobe, *SCCS*, (April 1987)
7. Waxy materials, *Vom Wax* **2** (122) 746-752 (1970)

Patents

8. French Patent 1,589,917 Film generating compositions for wound dressings (1967)
9. French Patent 2,017,419 Petroleum jelly substitute (1968)
10. German Patent 1,948,800 Bath additives, relubricating agents

Formula 7. Lipstick

Castor oil	24.60%
Isopropyl palmitate	22.00
Biosil Basics Fluoro Guerbet 3.5	12.00
PEG-4 diheptonate	4.00
Synthetic beeswax	8.00
Candelilla wax	6.60
Titanium dioxide	4.00
D&C red #6	4.60
Castor oil	8.80
Silica/mica	1.00
Propylparaben	0.20
BHT	0.10
Hexacaprylate/hexacaprate	4.10

Procedure: Into an appropriate kettle, add ingredients in order shown. Heat to 80 to 85°C under good agitation. Cool to 70 to 75°C and pour into suitable containers.

Sources

1. Biosil Technologies Inc., Englewood, NJ
Biosil Basics Fluoro Guerbet 3.5 provides thin non-occlusive film with good spreadability.

(1969)

11. German Patent 2,427,986 Soap and detergent bars, anti-cracking agents (1974)
12. German Patent 2,503,932 Powder in anti-perspirant sprays (1975)
13. US Patent 4,051,159 Transparent fragrance-releasing compounds (1976)
14. US Patent 4,868,483 assigned to Siltech (September 1989)
15. US Patent 5,321,968 assigned to Siltech (May 1994)
16. US Patent 5,235,017 (August 1993)



Formula 8. Oil-free "sport" makeup

A. Deionized water	56.40%
Magnesium aluminum silicate	0.30
Bentone	0.50
Methylparaben	0.30
B. Lecithin	0.20
Titanium dioxide	7.00
Iron oxide yellow	1.50
Iron oxide red	0.70
Iron oxide black	0.40
Nylon 12	2.00
C. Water	10.00
D. Triethanolamine, 99%	0.90
E. Lipovol MOS-70	10.00
Stearic acid	3.00
Glyceryl monostearate	1.50
Biosil Basics Fluoro Guerbet 3.5	2.00
Propylparaben	0.20
Isodecyl Citrate	1.50
F. Dimethyl Silanol Hyaluronate	0.50
G. Imidazolidinyl Urea	0.10
Water	1.00

Procedure: Into an appropriate kettle, add A in order shown. Add B, under agitation, in order shown. Pass AB through a colloid mill and recirculate until all pigments are evenly dispersed. Rinse colloid mill with C and heat to 80°C. Add D in order shown, maintaining temperature at 80°C. In a separate vessel, add E under agitation, heating to 80°C. Add premixed E to mixture under good agitation. Cool to 40°C. Add F and G. Cool to 30°C and pour into a suitable container.

Sources

1. Biosil Technologies Inc., Englewood, NJ
Biosil Basics Fluoro Guerbet 3.5 provides thin non-occlusive film with good spreadability.