A Review of Guerbet Chemistry

Anthony J. O'Lenick, Jr.

Guerbet alcohols have been known for over 100 years since Marcel Guerbet pioneered the basic chemistry in the 1890s. This chemistry has made possible the synthesis of a regiospecific, beta-branched hydrophobe which introduces high-purity branching into the molecule. The ability to capitalize upon this reaction sequence and develop derivatives has resulted in the preparation of many materials that find use in applications where liquidity and lubrication are important, such as in metal lubrication, plastic mold release, paper processing, synlube, and personal care products. The chemistry results in a unique class of materials that remain underutilized to this day.

GUERBET ALCOHOLS

CHEMISTRY

Guerbet alcohols are the oldest and best-understood material in the class of compounds, first synthesized by Marcel Guerbet The reaction sequence, which bears his name, is related to the Aldol Reaction and occurs at high temperatures under catalytic conditions. The overall reaction can be represented by the following equation;

$$2\ CH_3(CH_2)_9OH \xrightarrow[\text{Catalyst}]{\text{----------}} CH_3(CH_2)_9\underset{\displaystyle (CH_2)_7CH_3}{\underset{|}{C}}HCH_2OH$$

The product is an alcohol with twice the molecular weight of the reactant alcohol minus a mole of water. The reaction proceeds by a number of sequential steps:

A) oxidation of alcohol to aldehyde.

B) Aldol condensation after proton extraction.

C) dehydration of the Aldol product.

D) hydrogenation of the allylic aldehyde.

The following information is known about the sequence of reactions [2]

1. The reaction can take place without catalyst, but it is strongly catalyzed in the presence of hydrogen transfer catalysts.

2. At low temperatures of 130-140°C, oxidation process (i.e. formation of the aldehyde) is the rate-limiting step.

3. At somewhat higher temperatures of 160-180oC, the rate-limiting step is the Aldol Condensation.

4. At even higher temperatures, other degradative reactions occur and can become dominant.

Many catalysts have been described in the literature as effective for the preparation of Guerbet Alcohols. These include, nickel, lead salts (U.S. Patent 3,119,880), oxides of copper, lead, zinc, chromium, molybdenum, tungsten, and manganese (U.S. Patent 3,558,716). Later US patents (U.S. Patent 3,979,466) include palladium compounds and silver compounds (U.S. Patent 3,864,407). There are advantages and disadvantages for each type.

The Cannizzaro Reaction is a major side reaction and is described as the disproportionation of two molecules of an aldehyde brought about by the action of sodium or potassium hydroxide to yield the corresponding alcohol and acid. [4]

Raw Materials for the Preparation of Guerbet Alcohols

Most commonly used are alcohols of natural origin which are primary, with even-

numbered, straight carbon chains. Guerbet alcohols are beta-branched primary alcohols. Oxo alcohols can also be used, but both reaction rate and conversions are reduced.

Guerbet alcohols also are subjected to a series of post-reaction steps that (a) remove unreacted alcohol (vacuum stripping), (b) remove unsaturation (hydrogenation), (c) remove Cannizzaro soap (filtration) and (d) remove color/odor bodies. These operations add to the cost of the product but can be minimized or eliminated in many applications.

Guerbet Alcohol Properties

Because they are primary, branched, and of high molecular weight, Guerbet alcohols:

(1) have low irritation potential

(2) are liquid to extremely low temperatures.

(3) are low in volatility.

(4) are reactive and can be used to make many derivatives.

(5) are useful as superfatting agents.

(6) are good lubricants.

Guerbet alcohols are essentially saturated hence;

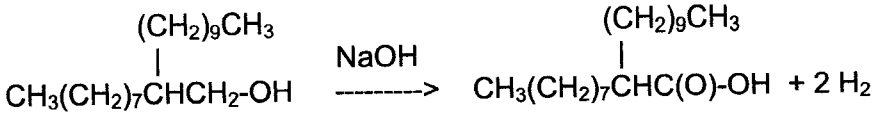
(1) they exhibit very good oxidative stability at elevated temperatures

(2) they have excellent color initially and at elevated temperatures

(3) they exhibit improved stability over unsaturated products in many applications.

GUERBET ACIDS

Guerbet acids are relatively new derivatives. They are prepared by the oxidation of Guerbet alcohols to produce primary carboxylic acids. Oxidative alkali fusion with alkali metal salts dehydrogenates the alcohol and gives excellent yields of carboxylic acids [6,7,8]



Octyldodecanol Octyldodecanoic Acid

The regiospecificity, purity and liquidity of the starting Guerbet acid make these materials good candidates for the evaluation of the effects of branching.

Guerbet alcohols as well as acids melt at lower temperatures than linear alcohols containing the same number of carbon atoms (Tables 1 and 2).

Table 1 B Melting Points of Various Alcohols

Carbon Number	Linear	Guerbet
C12	24° C	- 30°C
C16	50° C	- 18°C
C18	58° C	- 8°C
C20	62° C	0°C
C24	69° C	19°C

Compared to alcohols with the same number of carbon atoms, the

corresponding acids melt at higher temperatures. A carboxylic acid is able to form two hydrogen bonds with another acid, while the corresponding alcohol is able to form only one [9]

Table 2 B Melting Points of Various Acids

Carbon Number	Linear	Guerbet
12	44°C	- 15°C
16	63°C	17°C
20	75°C	35°C
24	84°C	48°C

GUERBET ESTERS

One of the desired effects of introducing Guerbet branching into ester molecules is to extend their liquidity to very low temperatures. With the availability of Guerbet acids and alcohols, branching can be introduced into (a) the alcohol, (b) the acid, or (c) both. [10]

In the determination of liquidity, the ester is heated to clarity and allowed to cool slowly until the first development of a haze of solid. This temperature is recorded as the titer point. Titer points can differ from solidification points in that some esters do not solidify, but turned into slushy semi-solids. Results are in Tables 3 and 4.

Table 3 B Esters with 32 Carbon Atoms

Designation	Acid Structure	Alcohol Structure	Appearance	Titer Point
Cetyl Palmitate	Linear	Linear	White Solid	34° C

Hexyldecyl Palmitate	Linear	Guerbet	Slushy Liquid	50° C
Cetyl Hexyldecanoate	Guerbet	Linear	Yellow Liquid	9° C
Hexyldecyl Hexyldecanoate	Guerbet	Guerbet	Yellow Liquid	< 0° C

Table 4 B Esters with 40 Carbon Atoms

Designation	Acid Structure	Alcohol Structure	Appearance	Titer Point
Eicosanyl Eicosanoate	Linear	Linear	White Solid	38° C
Octyldodecyl Eicosanoate	Linear	Guerbet	White Solid	48° C
Eicosan-e yl Octyldodecanoate	Guerbet	Linear	Yellow Liquid	34° C
Octyldodecyl Octyldodecanoate	Guerbet	Guerbet	Yellow Liquid	< 0° C

Products with the lowest titer carry Guerbet branching in both the acid and alcohol parts of the molecule. The next lowest titer point is obtained when the Guerbet branch is in the acid moiety. Branching in the alcohol part results in the highest titer. Products derived from linear acids and linear alcohols differ substantially from those derived from linear acids and Guerbet alcohols. Specifically, the former are rock hard solids while the latter are liquids with a snowy precipitate.

Solubilities

Solubilities of various Guerbet derivatives in several solvents are given in Tables 5 and 6.

Table 5 B Esters With 32 Carbon Atoms

Designation	Alcohol	Acid	A	B	C	D	E
Cetyl Palmitate	Linear	Linear	i	s	s	i	s
Hexyldecyl Palmitate	Linear	Guerbet	i	s	s	i	s

Cetyl Hexyldecanoate	Guerbet	Linear	i	s	s	i	s
Hexyldecyl hexyldecanoate	Guerbet	Guerbet	I	s	s	i	s

Table 6 B Esters With 40 Carbon Atoms

Designation	Alcohol	Acid	A	B	C	D	E
Eicosanyl Eicosanoate	Linear	Linear	i	s	s	i	s
Octyldodecyl Eicosanoate	Linear	Guerbet	i	s	s	i	s
Eicosan e yl Octyldodecanoate	Guerbet	Linear	i	s	s	i	s
Octyldodecyl Octyldodecanoate	Guerbet	Guerbet	I	s	s	i	s

Legend

A: water
B: isopropanol
C:cyclomethicone
D:dimethicone (350 Visc)
E: mineral oil

s = soluble
i = insoluble

Introduction of Guerbet branching into the ester molecule did not alter the solubility of the resultant ester.

Surfactant Derivatives

Guerbet Sulfates and Ether Sulfates

Sulfates and ether sulfates are workhorse anionic surfactants. One of the salient properties of a surfactant is the Krafft Point which is a measure of water solubility. It is defined as the temperature in °C at which a 1% dispersion becomes clear under gradual heat. The Krafft Point of sulfates rises with increasing molecular weight of the

hydrophobe or with the addition of propylene oxide to the hydrophobe. The Krafft Point decreases with addition of ethylene oxide. The Krafft Point provides another illustration of the differences between the linear and Guerbet-based sulfates. This is shown for sulfates in Table 7 and for ether sulfates in Table 8 below.

Table 7. B KRAFFT POINT o C B

Linear Alcohol Sulfate, Sodium Salt

Description	# Carbons	Krafft Point
Sodium lauryl sulfate	12	16 °C
Sodium myristyl sulfate	14	28 °C
Sodium cetyl sulfate	16	45 °C
Sodium stearyl sulfate	18	56 °C
Sodium oleyl sulfate	18 -	29°C

Guerbet Alcohol Sulfate, Sodium Salt

Sodium salt of sulfated octyldodecanol	20	insoluble

Table 8 B KRAFFT POINT oC

Ethoxylated Linear Alcohol Sulfate, Sodium Salt

Description	# Carbons in hydrophobe	Krafft Point
Sodium cetereth-3-sulfate	16	19 °C
Sodium cetereth-2-sulfate	16	24°C

Sodium steareth-3-sulfate	18	32°C
Sodium steareth-2-sulfate	18	40°C
Sodium oleth-3-sulfate	18 -	26°C
Sodium oleth-2-sulfate	18 -	40°C

Ethoxylated Guerbet Alcohol Sulfates, Sodium Salt

Sodium salt of sulfated octyldodecanol-3 EO	20	Insol.
Sodium salt of sulfated octyldodecanol-5 EO	20	Insol
Sodium salt of sulfated Octyldodecanol-12 EO	20	91°C
Sodium salt of sulfated octyldodecanol-15 EO	20	58°C
Sodium salt of sulfated octyldodecanol-20 EO	20	0°C

The location of the branch within the hydrophobe has a dramatic effect upon functional properties of anionic surfactants, such as their HLB and emulsifying power [11]. The introduction of branching can shift the HLB by as many as 3 units. This is thought to relate to twin tail structure of Guerbet-based surfactants which promotes their micellization in the oil phase. Twin tail surfactants require less cosurfactant to make microemulsions. Guerbet ether sulfates are very efficient emulsifiers for oil and emulsify three to five times more oil than the sulfates made from linear hydrophobes.

Patent Summary

The great versatility of Guerbet chemistry can be seen in the great diversity of United States patents covering new compositions of matter, applications and processes for making and using Guerbet derivatives.

Compounds (Composition of Matter)

1. 6,093,856 Polyoxyalkylene surfactants, issued July, 2000 inventors: Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth. Assigned Procter and Gamble Co.

2. 6,060,443 Mid-chain branched alkyl sulfate surfactants, issued May, 2000 inventors; Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth. Assigned Procter and Gamble Co.

3. 6,013,813 Guerbet based sorbitan esters, issued Jan. 2000, inventor; O'Lenick, Jr. Anthony, assigned to Hansotech Inc.

4. 6,008,181 Mid-Chain branched Alkoxylated Sulfate Surfactants, issued Dec, 1999 inventors: Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth. Assigned Procter and Gamble Co.

5. 5,929,263 Guerbet branched quaternary compounds, issued Jul 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc..

6. 5,919,959 Guerbet branched amine oxides, issued Jul 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.

7. 5,919,743 Guerbet branched quaternary compounds in personal care applications, issued Jul 1999, inventor; O'Lenick, Jr. Anthony, assigned to Petroferm Inc.

8. 5,786,389 Guerbet castor esters, issued Jul 1999, inventors; O'Lenick, Jr. Anthony; Parkinson, Jeff K. assigned to Lambent Technologies Inc.

9. 5,756,785 Guerbet betaines, issued May 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.

10. 5,744,626 Complex Guerbet acid esters, issued April 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.

11. 5,717,119 Polyoxyalkylene glycol Guerbet esters, issued February 1999, inventor; O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc.

12. 5,646,321 Guerbet meadowfoam esters, issued Jul 1997, inventor; O'Lenick, Jr. Anthony, assigned to Siltech Inc.

13. 5,488,121 Di-Guerbet esters, issued Jan 1996, inventor; O'Lenick, Jr. Anthony, assigned to Siltech Inc.

14. 5,387,374 Guerbet carbonates, issued Feb 1995, inventors Westfechtel, Alfred; Bongardt, Frank; Ansmann, Achim, assigned to Henkel KgaA

15. 5,312,968 Fluorine containing Guerbet citrate esters, issued May 1994, inventors; O'Lenick, Jr. Anthony, and Buffa, Charles W., assigned to Siltech Inc. and Biosil Technologies Inc.

16. 5,264,006 Guerbet alkyl ether monoamines, issued Nov. 1993, inventors; Schilowitz, Alan; Krogh, James; Mokadam, Anita; Clumpner, Michael; and Berlowitz, Paul, assigned to Exxon Research.

17. 5,094,667 Guerbet alkyl ether mono amines, issued Mar. 1992, inventors; Schilowitz, Alan; Krogh, James; Mokadam, Anita; Clumpner, Michael; and Berlowitz, Paul, assigned to Exxon Research.

18. 4,830,769 Propoxylated Guerbet alcohols and esters thereof , issued May 1989, inventors; O'Lenick, Jr. Anthony, and Bilbo, Raymond Edward, assigned to GAF Corporation.

19. 4,800,077 Guerbet quaternary compounds, issued Jan1989, inventors; O'Lenick, Jr. Anthony, and Smith, Wayne C., assigned to GAF Corporation.

20. 4,767,815 Guerbet alcohol esters, issued Aug 1988, inventor; O'Lenick, Jr. Anthony, assigned to GAF Corporation.

21. 4,731,190 Alkoxylated Guerbet alcohols and esters as metal working lubricants, issued Jan1984, inventor; O'Lenick, Jr. Anthony, assigned to Alkaril Chemicals Inc.

22. 4,425,458 Polyguerbet alcohol esters, issued Jan1984 inventors; Lindner, Robert and O'Lenick, Jr. Anthony, assigned to Henkel Corporation.

Applications (Formulations)

1. 6,087,309 Liquid cleaning compositions containing selected mid-chain branched surfactants- issued Jul 2000, inventors Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter and Gamble Co.

2. 6,046,152 Liquid cleaning compositions containing selected mid-chain branched surfactants, issued Apr 2000, inventors Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter and Gamble Co.

3. 6,036,947 Transfer resistant high lustre lipstick compositions, issued Mar 2000, inventors Barone, Salvatore; Krog, Ann; Jose, Natividad and Ordino, Renee, assigned to Revlon Consumer Products Co.
4. 6,015,781 Detergent compositions containing selected mid-chain branched surfactants , issued Jan 0, inventors Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter and Gamble Co.

5. 5,837,223 Transfer resistant high lustre cosmetic stick compositions, issued Nov 1998, inventors Barone, Salvatore; Krog, Ann; Jose, Natividad and Ordino, Renee, assigned to Revlon Consumer Products Co.

6. 5,736,571 Guerbet meadowfoam esters in personal care, issued Apr 1998, inventor O'Lenick, Jr. Anthony, assigned to Lambent Technologies Inc and FanTech Ltd.

7. 5,709,739 Release agents for hydraulic binders, - issued Jan 1998, inventors Wittich, Leonhard; Heck, Stephan; Freichenhagen Lothar; Demmering, Guenther; Komp, Horst; Koehler, Michael; Wegener, Ingo and Sladek, Hans, assigned to Henkel Kgaa.

8. 5,686,087 Cosmetic and/or pharmaceutical formulations with an improved feeling on the skin based on mixed Guerbet alcohols, issued Nov 1997, inventors Ansmann, Achim; Kawa, Rolf; Mohr, Klaus and Koester Josef, not assigned.

9. 5,677,436 Process for making alkyl polyglcosides having improved aesthetic and tactile
properties, issued Oct 1997, inventors Desai, S; Hessel, Fred; John; Urfer, Allen and Allen, Charles, assigned to Henkel Corporation.

10. 5,663,117 Alkoxylated primary alcohol surfactants providing enhanced efficacy and/or rainfastness to glyphosate formulations - issued Sept 1997 inventor Warner, James assigned to Monsanto Co.

11. 5,656,200 Foaming emulsions- issued Aug 1997, inventors Boettcher, Axel; Hensen, Hermann; Seipel, Werner; Tesmann, Holger, assigned to Henkel KGaA.

12. 5,639,791 Di-Guerbet esters in personal care applications - issued Jun 1997. Inventor O'Lenick, Anthony J. assigned to Siltech Inc.

13. 5,605,683 Alkyl polyglycosides in hair skin cleansing compositions- issued Feb 1997, inventors Desai, Sureshchandra; Hessel, Fred; Urfer, Allen; Allen, Charles; Assigned to Henkel Corporation.

14. 5,567,808 Alkyl polyglycosides having improved aesthetic and tactile properties issued Feb 1997, inventors Desai, Sureshchandra; Hessel, Fred; Urfer, Allen; Allen, Charles; Assigned to Henkel Corporation.

15. 5,494,938 Oil-in-water emulsions -issued Feb 1996, inventors Kawa, Rolf; Ansmann, Achim; Wuerth, Manfred; Tessman, Holger; Foerster, Thomas, assigned to Henkel Kgaa.

16. 5,476,517 Use of Guerbet alcohols for preventing fatty spew on leather - issued Dec 1995, inventors Zauns-Huber, Ruldolf; Ruschensky, Emil; Wolter, Fredi, assigned to Henkel KGaA.

17. 5,421,907 Process for cold cleaning oil-contaminated metal surfaces with 2-ethylhexyl esters of fatty acids - issued Jun 1995 inventors Nieendick, Claus; Schmid, Karl; Mueller, Heinz; Herold, Claus-Peter, assigned to Henkel KGaA.

19. 5,360,560 Universal lubricant based on a synthetic oil solution - issued Nov 1994, inventors Schmid, Karl; Bongardt, Frank; Roeder, Juergen; Wuest, Reinhold, assignet to Henkel KGaA.

20. 5,298,038 Guerbet branched alkoxylated amine detergent additives - issued Mar 1994, inventor Hashimoto, Jiro; Nomoto, Shogo; assigned to Kao Corporation.

21. 5,286,397 Base oil for the lubricant industry - issued Feb 1994, inventor Schmid, Karl; Bongardt, Frank; Wuest, Reinhold, assigned to Henkel KGaA.

22. 5,238,985 Thermoplastic molding compositions- issued Aug 1993, inventor O'Lenick, Anthony J., assigned to Rhone Poulenc Surfactants and Specialities.

Conclusion

Guerbet chemistry offers a unique set of starting materials for the preparation of highly effective surfactants and specialty materials for a variety of markets. Although the basic chemistry has been known for one hundred years, the application of these materials in high performance products is a relatively new phenomenon as evidenced by the patent literature.

The effect of branching on the performance properties of Guerbet surfactants will result in continuing commercial development of products based upon this chemistry. The high cost of Guerbet products will, however, cause these products to remain limited to high-performance specialties where cost performance rather than just cost per pound will dictate what is sold.

References

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