Guerbet Chemistry

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ABSTRACT: Although the chemistry named after Marcel Guerbet was developed over 100 yr ago, Guerbet alcohols, Guerbet acids, and derivatives based upon them remain a topic of continued interest because of their (i) unique branching pattern, both in terms of size of the branch group and purity of the compounds, (ii) oxidative stability, and (iii) liquidity of the products. This review article is offered to demonstrate the diversity of chemistry possible using these materials and the large variety of applications for which these compounds are useful.

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KEY WORDS: Aldol condensation, branched alcohols, Cannizzaro reaction, Guerbet acids, Guerbet alcohols, Guerbet esters, Guerbet patents, Guerbet reaction, Guerbet sulfates, octyldodecanol.

Guerbet alcohols have been known since Marcel Guerbet pioneered the basic chemistry in the 1890s. This chemistry has made possible the synthesis of a regiospecific, β-branched hydrophobe, which introduces branching with a very high degree of regiospecificity 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, synthetic lubricants (synlube), and personal-care products. The chemistry results in a unique class of materials that remain underutilized to this day.

GUERBET ALCOHOLS

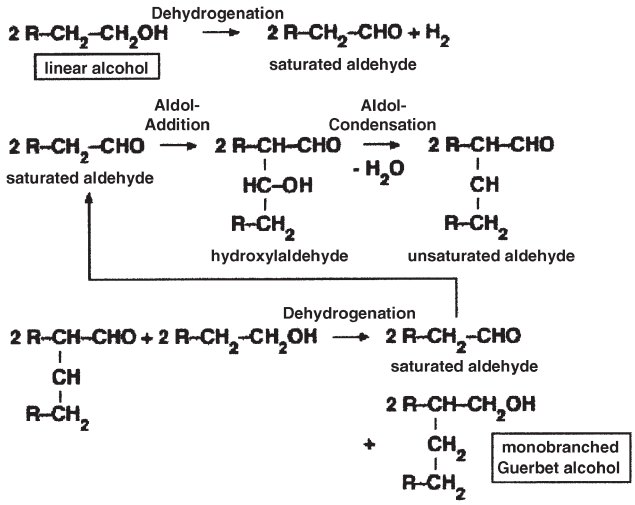
Chemistry. Guerbet alcohols are the oldest and best-understood material in the class of compounds first synthesized by Marcel Guerbet (1). The reaction sequence, which bears his name, is related to the aldol reaction and occurs at high temperatures under catalytic conditions. The overall reaction can be represented by Equation 1.

$$2\ CH_3(CH_2)_9OH \xrightarrow[\text{Catalyst}]{} CH_3(CH_2)_9CH(CH_2)_7CH_3\text{-}CH_2OH \quad [1]$$

The product is a β-branched primary alcohol with twice the molecular weight of the reactant alcohol minus a mole of water. The reaction proceeds by a number of sequential steps: (i) oxidation of alcohol to aldehyde, (ii) aldol condensation after proton extraction, (iii) dehydration of the aldol product, and (iv) hydrogenation of the allylic aldehyde (Scheme 1).

The following information is known about the sequence of reactions (2):

- The reaction can take place without a catalyst, but it is strongly catalyzed in the presence of hydrogen transfer catalysts.
- At low temperatures (130–140°C), the oxidation process (i.e., formation of the aldehyde) is the rate-limiting step.



SCHEME 1. Guerbet reaction sequence. *Source*: Condea Vista, Austin, TX.

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- At somewhat higher temperatures (160–180°C), the rate-limiting step is the aldol condensation.
- 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 including, nickel, lead salts (U.S. Patent 3,119,880), and oxides of copper, lead, zinc, chromium, molybdenum, tungsten, and manganese (U.S. Patent 3,558,716). Later U.S. patents include palladium compounds (U.S. Patent 3,979,466) and silver compounds (U.S. Patent 3,864,407). There are advantages and disadvantages for each type.

The Cannizzaro reaction (3) 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. The most commonly used raw materials are primary alcohols of natural origin, with even-numbered, straight carbon chains. Oxo alcohols can also be used, but both reaction rate and conversions are reduced.

Guerbet alcohols can be subjected to a series of postreaction steps that (i) remove unreacted alcohol (vacuum stripping), (ii) remove unsaturation (hydrogenation), (iii) remove Cannizzaro soap (filtration), and (iv) 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 have low irritation potential, are liquid to extremely low temperatures, have low volatility, are reactive and can be used to make many derivatives, are useful as superfatting agents, and are good lubricants. Guerbet alcohols are essentially saturated, hence they exhibit very good oxidative stability at elevated temperatures, have excellent color initially and at elevated temperatures, and 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 (Eq. 2). Oxidative alkali fusion with alkali metal salts dehydrogenates the alcohol and gives excellent yields of carboxylic acids (6–8).

$$\begin{array}{l} \quad\quad (CH_2)_9CH_3 \qquad\qquad\quad (CH_2)_9CH_3 \\ \quad\quad\ \ | \qquad\quad NaOH \qquad\quad\ \ | \qquad\qquad [2] \\ CH_3(CH_2)_7CHCH_2OH \longrightarrow CH_3(CH_2)_7CHC(O)OH + 2\,H_2 \\ \text{Octyldodecanol} \qquad\quad \text{Octyldodecanoic acid} \end{array}$$

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 (Table 1).

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).

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 the alcohol, the acid, or 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 because some esters do not solidify, but turn into slushy semisolids. Examples are illustrated in Tables 2 and 3.

Esters with the lowest titer points carry Guerbet branching in both the acid and alcohol parts of the molecule. The next-lowest titer points are obtained when the Guerbet branch is in the acid moiety. Branching in the alcohol part results in the highest titer. Esters 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 esters in several solvents are given in Tables 4 and 5. Introduction of Guerbet branching into the ester molecule does 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 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 linear and Guerbet-based sulfates (Tables 6, 7).

The location of the branch within the hydrophobe has a dramatic effect upon functional properties of anionic surfactants, such as their hydrophilic-lipophilic balance (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 the 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

TABLE 1
Melting Points (°C) of Various Alcohols and Acids

Carbon number	Alcohol		Acid	
	Linear	Guerbet	Linear	Guerbet
C12	24	–30	44	–15
C16	50	–18	63	17
C18	58	–8	69	27
C20	62	0	75	35
C24	69	19	84	48

TABLE 2
Appearance and Titer Points (°C) of Esters with 32 Carbon Atoms

Designation	Acid structure	Alcohol structure	Appearance[a]	Titer point
Cetyl palmitate	Linear	Linear	White solid	34
Hexyldecyl palmitate	Linear	Guerbet	Slushy liquid	50
Cetyl hexyldecanoate	Guerbet	Linear	Yellow liquid	9
Hexyldecyl hexyldecanoate	Guerbet	Guerbet	Yellow liquid	0

[a]At the titer point.

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 to Procter & 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 to Procter & Gamble Co.
3. 6,013,813 Guerbet based sorbitan esters, issued January 2000. Inventor: O'Lenick, Anthony, Jr., assigned to Hansotech Inc.
4. 6,008,181 Mid-chain branched alkoxylated sulfate surfactants, issued December 1999. Inventors: Cripe, Thomas; Conner, Daniel; Vinson, Phillip; Burckett, Laurent; James, Charles; Willman, Jenneth, assigned to Procter & Gamble Co.
5. 5,929,263 Guerbet branched quaternary compounds, issued July 1999. Inventor: O'Lenick, Anthony, Jr., assigned to Lambent Technologies Inc.
6. 5,919,959 Guerbet branched amine oxides, issued July 1999. Inventor: O'Lenick, Anthony, Jr., assigned to Lambent Technologies Inc.
7. 5,919,743 Guerbet branched quaternary compounds in personal care applications, issued July 1999. Inventor: O'Lenick, Anthony, Jr., assigned to Petroferm Inc.
8. 5,786,389 Guerbet castor esters, issued July 1999. Inventors: O'Lenick, Anthony, Jr., Parkinson, Jeff K., assigned to Lambent Technologies Inc.
9. 5,756,785 Guerbet betaines, issued May 1999. Inventor: O'Lenick, Anthony, Jr., assigned to Lambent Technologies Inc.
10. 5,744,626 Complex Guerbet acid esters, issued April 1999. Inventor: O'Lenick, Anthony, Jr., assigned to Lambent Technologies Inc.
11. 5,717,119 Polyoxyalkylene glycol Guerbet esters, issued February 1999. Inventor: O'Lenick, Anthony, Jr., assigned to Lambent Technologies Inc.
12. 5,646,321 Guerbet meadowfoam esters, issued July 1997. Inventor: O'Lenick, Anthony, Jr., assigned to Siltech Inc.
13. 5,488,121 Di-Guerbet esters, issued January 1996. Inventor: O'Lenick, Anthony, Jr., assigned to Siltech Inc.
14. 5,387,374 Guerbet carbonates, issued February 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, Anthony, Jr.; Buffa, Charles W., assigned to Siltech Inc. and Biosil Technologies Inc.
16. 5,264,006 Guerbet alkyl ether monoamines, issued November 1993. Inventors: Schilowitz, Alan; Krogh, James; Mokadam,

TABLE 3
Appearance and Titer Points (°C) of Esters with 40 Carbon Atoms

Designation	Acid structure	Alcohol structure	Appearance[a]	Titer point
Eicosanyl eicosanoate	Linear	Linear	White solid	38
Octyldodecyl eicosanoate	Linear	Guerbet	White solid	48
Eicosanoyl octyldodecanoate	Guerbet	Linear	Yellow liquid	34
Octyldodecyl octyldodecanoate	Guerbet	Guerbet	Yellow liquid	< 0

[a]At the titer point.

TABLE 4
Solubilities[a] of 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

[a]Abbreviations: A, water; B, isopropanol; C, cyclomethicone; D, dimethicone with a viscosity of 350 centipoises; E, mineral oil; s, soluble; i, insoluble.

TABLE 5
Solubilities of 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
Eicosanoyl octyldodecanoate	Guerbet	Linear	i	s	s	i	s
Octyldodecyl octyldodecanoate	Guerbet	Guerbet	I	s	s	i	s

[a]For abbreviations see Table 4.

TABLE 6
Krafft Point (°C) of Some Alcohol Sulfates

Description	# Carbons	Krafft point
Linear alcohol sulfate, sodium salt		
Sodium lauryl sulfate	12	16
Sodium myristyl sulfate	14	28
Sodium cetyl sulfate	16	45
Sodium stearyl sulfate	18	56
Sodium oleyl sulfate	18	29
Guerbet alcohol sulfate, sodium salt		
Sodium salt of sulfated octyldodecanol	20	Insoluble

TABLE 7
Krafft Point (°C) of Some Ethoxylated Alcohol Sulfates[a]

Description	# Carbons in hydrophobe	Krafft point
Ethoxylated linear alcohol sulfate, sodium salt		
Sodium cetereth-3-sulfate	16	19
Sodium cetereth-2-sulfate	16	24
Sodium steareth-3-sulfate	18	32
Sodium steareth-2-sulfate	18	40
Sodium oleth-3-sulfate	18	26
Sodium oleth-2-sulfate	18	40
Ethoxylated Guerbet alcohol sulfates, sodium salt		
Sodium salt of sulfated octyldodecanol-3 EO	20	Insoluble
Sodium salt of sulfated octyldodecanol-5 EO	20	Insoluble
Sodium salt of sulfated octyldodecanol-12 EO	20	91
Sodium salt of sulfated octyldodecanol-15 EO	20	58
Sodium salt of sulfated octyldodecanol-20 EO	20	0

[a]EO, ethylene oxide.

Anita; Clumpner, Michael; and Berlowitz, Paul, assigned to Exxon Research.
17. 5,094,667 Guerbet alkyl ether mono amines, issued March 1992. Inventors: Schilowitz, Alan; Krogh, James; Mokadam, Anita; Clumpner, Michael; Berlowitz, Paul, assigned to Exxon Research.
18. 4,830,769 Propoxylated Guerbet alcohols and esters thereof, issued May 1989. Inventors: O'Lenick, Anthony, Jr.; Bilbo, Raymond Edward, assigned to GAF Corporation.
19. 4,800,077 Guerbet quaternary compounds, issued January 1989. Inventors: O'Lenick, Anthony, Jr.; Smith, Wayne C., assigned to GAF Corporation.
20. 4,767,815 Guerbet alcohol esters, issued August 1988. Inventor: O'Lenick, Anthony, Jr., assigned to GAF Corporation.
21. 4,731,190 Alkoxylated Guerbet alcohols and esters as metal working lubricants, issued January 1984. Inventor: O'Lenick, Anthony, Jr., assigned to Alkaril Chemicals Inc.
22. 4,425,458 Polyguerbet alcohol esters, issued January 1984. Inventors: Lindner, Robert; O'Lenick, Anthony, Jr., assigned to Henkel Corporation.

Applications (formulations)

1. 6,087,309 Liquid cleaning compositions containing selected mid-chain branched surfactants, issued July 2000. Inventors: Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter & Gamble Co.
2. 6,046,152 Liquid cleaning compositions containing selected mid-chain branched surfactants, issued April 2000. Inventors: Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter & Gamble Co.
3. 6,036,947 Transfer resistant high lustre lipstick compositions, issued March 2000. Inventors: Barone, Salvatore; Krog, Ann; Jose, Natividad; Ordino, Renee, assigned to Revlon Consumer Products Co.
4. 6,015,781 Detergent compositions containing selected mid-chain branched surfactants, issued January 2000. Inventors: Vinson, Phillip; Foley, Peter; Cripe, Thomas; Connor, Daniel, assigned to Procter & Gamble Co.
5. 5,837,223 Transfer resistant high lustre cosmetic stick compositions, issued November 1998. Inventors: Barone, Salvatore; Krog, Ann M.; Jose, Natividad; Ordino, Renee M., assigned to Revlon Consumer Products Co.
6. 5,736,571 Guerbet meadowfoam esters in personal care, issued April 1998. Inventor: O'Lenick, Anthony, Jr., assigned to Lambent Technologies Inc. and FanTech Ltd.
7. 5,709,739 Release agents for hydraulic binders, issued January 1998. Inventors: Wittich, Leonhard; Heck, Stephan; Freichenhagen, Lothar; Demmering, Guenther; Komp, Horst; Koehler, Michael; Wegener, Ingo; 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 November 1997. Inventors: Ansmann, Achim; Kawa, Rolf; Mohr, Klaus; Koester, Josef, not assigned.
9. 5,677,436 Process for making alkyl polyglycosides having improved aesthetic and tactile properties, issued October 1997. Inventors: Desai, S.; Hessel, John F.; Urfer, Allen D.; Allen, Charles B., assigned to Henkel Corporation.
10. 5,663,117 Alkoxylated primary alcohol surfactants providing enhanced efficacy and/or rainfastness to glyphosate formulations, issued September 1997. Inventor: Warner, James, assigned to Monsanto Co.
11. 5,656,200 Foaming emulsions, issued August 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 June 1997. Inventor: O'Lenick, Anthony J., assigned to Siltech Inc.
13. 5,605,683 Alkyl polyglycosides in hair skin cleansing compositions, issued February 1997. Inventors: Desai, Sureshchandra; Hessel, John F.; Urfer, Allen D.; Allen, Charles B., assigned to Henkel Corporation.
14. 5,567,808 Alkyl polyglycosides having improved aesthetic and tactile properties, issued February 1997. Inventors: Desai, Sureshchandra; Hessel, Fred; Urfer, Allen; Allen, Charles, assigned to Henkel Corporation.
15. 5,494,938 Oil-in-water emulsions, issued February 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 December 1995. Inventors: Zauns-Huber, Rudolf; 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 June 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 November 1994. Inventors: Schmid, Karl; Bongardt, Frank; Roeder, Juergen; Wuest, Reinhold, assigned to Henkel KGaA.
20. 5,298,038 Guerbet branched alkoxylated amine detergent ad-

ditives, issued March 1994. Inventors: Hashimoto, Jiro; Nomoto, Shogo, assigned to Kao Corporation.
21. 5,286,397 Base oil for the lubricant industry, issued February 1994. Inventors: Schmid, Karl; Bongardt, Frank; Wuest, Reinhold, assigned to Henkel KGaA.
22. 5,238,985 Thermoplastic molding compositions, issued August 1993. Inventor: O'Lenick, Anthony J., assigned to Rhône-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 100 yr, 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.

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