GUERBET ALCOHOLS

A Versatile Hydrophobe

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Guerbet alcohols have been known since the 1890's when Marcel Guerbet (1) first synthesized these compounds. The reaction sequence that bears his name is related to the aldol condensation and occurs at high temperatures in the presence of alkaline catalysts. The overall reaction can be represented by the following equation:

$$2\ RCH_2CH_2OH \xrightarrow[\text{Catalyst}]{\Delta} \underset{|}{\overset{R}{}}RCHCH_2OH$$

The product is an alcohol with essentially double molecular weight. The reaction proceeds by a number of sequential steps (Figure 1). These steps are: (1) oxidation of the alcohol to an aldehyde; (2) aldol condensation of the aldehyde; (3) dehydration of the aldol product; and (4) hydrogenation and reduction of the allylic aldehyde.

The following has been established about the Guerbet sequence of reactions: (2)

(1) The reaction takes place without catalyst, but is strongly catalysed by addition of hydrogen transfer catalysts.

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

(3) At somewhat higher temperatures (160-180°C), 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 U.S. patents (3,979,466) include palladium compounds and silver compounds (3,864,407). There are advantages and disadvantages with each type of catalyst.

The Cannizzaro reaction, (3) a major side reaction, is 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) It can be represented by the following equation:

$$2\ RCH_2COH \xrightarrow[\text{Heat}]{KOH} RCH_2COOK \text{ and } RCH_2CH_2OH$$

Both natural and synthetic alcohols may be used as raw materials for Guerbet alcohol synthesis. Synthetic alcohols are, by definition, not derived from fats and may also be branched, odd-carbon or secondary alcohols. The candidates of interest for the commercial production of guerbet alcohols are primary alcohols.

Oxo alcohols and unsaturated alcohols may also be used. The use of an unsaturated alcohol (i.e. oleyl) results in a product having a total of 36 carbons and still remaining liquid.

General Properties

A. Guerbet alcohols have high molecular weight, hence:

(1) They have low irritation properties.

(2) They are branched, therefore, they are liquid to extremely low temperatures (Figure 2).

(3) They have low volatility.

Figure 1
Guerbet Reaction Sequence

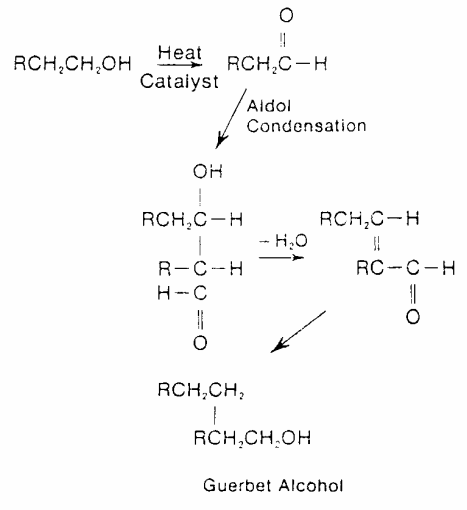
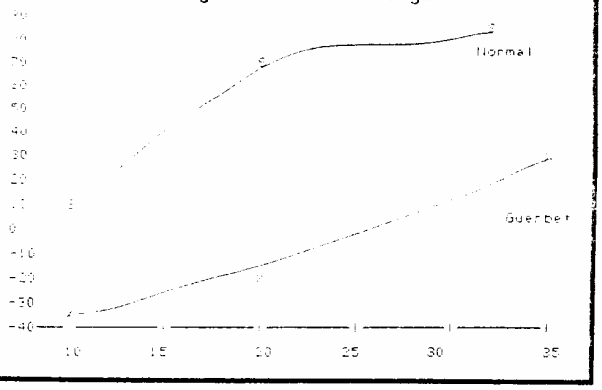


Figure 2
Melting Point vs. Chain Length



(4) They are primary alcohols, so are reactive and can be used to make many derivatives.

(5) They are useful as superfatting agents to re-oil the skin and hair.

(6) They are good lubricants.

B. 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.

Among the available guerbet alcohol products are:

Product	Name
Guerbet (20) branched	Alkol GB-20
Guerbet (20) normal	Alkol G-20
Guerbet (16) normal	Alkol G-16
Guerbet (24-26) normal	Alkol G-246

Guerbet Alcohol Applications

(1) Foam inhibitors in antifreeze. U.S. Patent 3,334,260, 1965.

(2) Water vapor porosity increase of fats. U.S. Patent 3,335,053, 1965.

(3) Rubber-like yarn lubricants. U.S. Patent 3,368,917, 1968.

(4) Pour point modifiers. Petrochem. 1970,23 (22), 94-97.

(5) Dyeing and printing of wool. French Patent 1,534,471, 1965.

(6) Film generating compositions for wound dressings. French Patent 1,589,917, 1967.

(7) Bath additives, relubricating agents. German Patent 1,948,800, 1969.

(8) Waxy materials. Vom Wax 1970, 2, (122), 746-752.

(9) Petroleum jelly substitute, French Patent 2,017,419, 1968.

(10) Lipsticks, resin based. Japan 70 41,318, 12/1970.

(11) Aerosol antiperspirant. Cosmet. Perfum. 1973, 88 (5), 35-38.

(12) Dishwash rinse aides. German Patent 2,213,007, 1972.

(13) Superfatting shampoo additive. Cosmet. Perfum. 1973, 88 (8), 35-38.

(14) Detergent anti-graying agents. German Patent 2,243,307, 1974.

(15) Lipsticks. Cosmet. Perfum. 1975, 90 (1), 31-35.

(16) Soap and detergent bars, anti-cracking agents. German Patent 2,427,986, 1974.

(17) Powder in antiperspirant sprays. German Patent 2,503,923.

(18) Transparent fragrance releasing compounds. U.S. Patent 4,051,159, 1976.

(19) Plastic lubricant. U.S. Patent 4,425,458, 1984.

(20) Compression mold cleaning. German Patent 2,647,447, 1978.

(21) Soil release agents. U.S. Patent 4,108,780, 1978.

Guerbet Alcohol Derivatives

Guerbet alcohols contain a primary hydroxyl group and can be substitutes for fatty alcohols in many reaction sequences to give improved functional properties. These properties include decreased volatility, higher liquidity at a given number of carbon atoms, increased lubrication and generally lower irritation due to the high molecular weight.

Esters

Fatty esters are generally prepared by reacting an alcohol and a carboxylic acid at elevated temperatures. The reaction proceeds with removal of water and may be represented as follows:

ROH	+ R'COOH	⟶	R'COOR	+ HOH
Guerbet	Organic Acid		Ester	Water

Several products have been developed and evaluated in a number of applications. They are:

Product	Name
Guerbet (20) adipate	Alkalube G GDA
Guerbet (20) stearate	Alkalube G GS
Guerbet (20) dimerate	Alkalube G GDD

These products are liquid at low temperatures and are used in various lubricant applications, including but not limited to fiber, metal and synthetic lubrication.

Surfactants

In order to obtain a product with surface activity, it is necessary to have a hydrophobic and hydrophilic portion within the molecule. The hydrophobe or fatty soluble portion of the molecule comes from the guerbet alcohol chosen. If the hydrophobic portion of the molecule is too high in molecular weight, a water insoluble, oil soluble product is produced which has essentially no surface activity. This is the case with guerbet esters.

HLB is the so called hydrophile-lipophile balance and relates the ratio of the oil soluble to water soluble portion of a molecule. The system was originally developed for ethoxylated products. It was expanded several times to include other classes of surface active agents.

Table I gives some approximations for the HLB value of surfactants as a function of their solubility in water. These are only approximations.

Table I

Solubility in Water	HLB Value	Description
Insoluble	4-5	water-in-oil emulsions
Poorly dispersible (milky appearance)	6-9	wetting agent
Translucent to clear	10-12	detergent
Very soluble	13-18	oil-in-water emulsion

Table II
Properties of Selected Surfactants

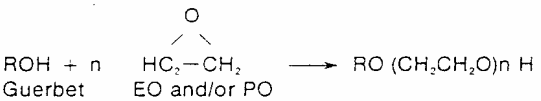
Name	HLB	Mol. Wt.
Alkasurf G E-3	5	430
Oil soluble emulsifier and coupler.		
Alkasurf G E-5	10	518
Water dispersible emulsifier O/W		
Alkasurf G E-20	15	1178
Oil-in-water emulsifier		

Surfactant Properties
Conventional Surfactants

Name	HLB	Mol. Wt.
Alkamuls SMO	4.3	362
(sorbitan mono oleate)		
Oil soluble emulsifier and coupler		
Alkasurf NP-9	13.4	638
(nonyl phenol 9 EO)		
Detergent		
Alkasurf DA-3	9	290
(decyl alcohol 3)		
Water dispersible emulsifier		
Alkasurf DA-5	11.6	378
(decyl alcohol 5)		
Oil-in-water emulsifier		
Alkasurf DA-20	17.4	1012
(decyl alcohol 20)		
Detergent		

Alkoxylation

A surfactant can be made by the ethoxylation or propoxylation of a guerbet alcohol to obtain essentially any HLB desired.



Several products based upon the above reaction sequence have been developed. The following are examples:

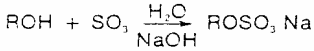
Product	Name
Guerbet (20) 3 EO	Alkasurf G E-3
Guerbet (20) 5 EO	Alkasurf G E-5
Guerbet (20) 20 EO	Alkasurf G E-20
Guerbet (20) 3 EO, 2 PO	Alkasurf G E3-P2

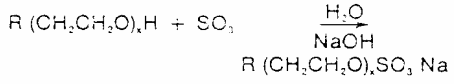
Some properties of these materials along with those of more conventional surfactants are shown in Table II.

Sulfates and Ether Sulfates

The alcohols can be sulfated as prepared or ethoxylated to give a chosen HLB value.

The reaction sequence is as follows:





Sulfates and ether sulfates are very important classes of surface active agents. Their importance in the personal care area becomes clear when one considers that all of the top 10 shampoos contain sulfates.

In the evaluation of a given sulfate, there are a variety of possible functional attributes that can be considered. One is a measure of water solubility called **Krafft Point.** It is defined as the temperature in degrees centigrade at which a one percent dispersion becomes clear under gradual heat. Krafft point will increase as one increases the molecular weight of the hydrophobe being sulfated, or as one adds propylene oxide to the hydrophobe (Table III). Krafft point will decrease with addition of ethylene oxide to the molecule (Table IV).

Table III
Krafft Point °C.
Linear Alcohol Sulfates, Sodium Salt

Description	# Carbons	Krafft Point
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
Sodium salt of sulfated Alkol G-20	20	Insoluble

Krafft Point °C.
Linear Alcohol Sulfates, Sodium Salt

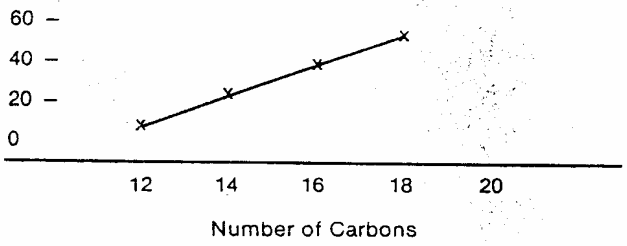


Table IV
Krafft Point °C.
Ethoxylated Linear Alcohol Sulfates, Sodium Salt

Description	# Carbons in hydrophobe	Krafft Point
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
Sodium salt of sulfated Alkasurf G E-3	20	Insol.
Sodium salt of sulfated Alkasurf G E-5	20	Insol.
Sodium salt of sulfated Alkasurf G E-12	20	91
Sodium salt of sulfated Alkasurf G E-15	20	58
Sodium salt of sulfated Alkasurf G E-20	20	0

The Guerbet derivatives with their high molecular weight and branching have very high Krafft points. The addition of ethylene oxide will lower the Krafft point (i.e., the material becomes more water soluble). The addition of five moles of ethylene oxide on Alkol G-20 will result in a sulfate that resembles sodium lauryl sulfate in viscosity performance and foam in a simple shampoo system. Five moles of ethylene oxide on lauryl alcohol will produce a surfactant that is too water soluble to give the desired foam and viscosity performance (Figure 3).

There has been a recent trend toward using the higher ethoxylated lauryl alcohol in shampoo formulations to achieve lower irritation scores by increasing molecular weight. This might be accomplished, without the negative effects of the low viscosity performance, by using a guerbet ethoxy-sulfate.

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Weathering Machine

Louis P. Batson, Inc., Greenville, S.C. offers the Batson/Original Hanau Suntest Exposure Machine for testing the light stability of cosmetics, chemicals and other products. The unit uses radiation distribution similar to sunlight that is said to correlate well with outdoor exposure results. The table unit is equipped with a low-pressure Xenon burner and offers variable high ultraviolet intensity levels.

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Guerbet Alcohols

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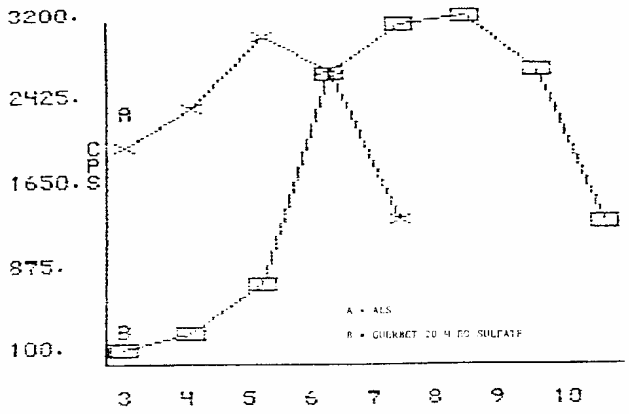
In summary, guerbet alcohols offer the potential benefits of high molecular weight, branching, liquidity and ability to be used in derivatives as very hydrophobic raw materials. Since one can add relatively large amounts of ethylene oxide to guerbets to achieve the performance of traditional fatty alcohol surfactants and since new technology has been developed that makes guerbets more cost effective, these materials should find more use in the personal care field.

Figure 3
Viscosity Performance vs. % Sodium Chloride



Formulation	
Alkamide CDO	2.0
Sodium Chloride	1.0
Sulfated product	40.0
Water	qs

References

(1) M. Guerbet, C.R. Acad. Sci. Paris, 128, 511; 1002 (1899).

(2) Veibel, S. and Nielsen, J. Tetrahedrone, 23, 1723-1733 (1967).

(3) S. Cannizzaro, Ann. Chem. Liebigs, 88, 129, (1853).

(4) Geissman, T.A., Organic Reactions, Vol. II, P. 94, Wiley, New York (1944).

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