Guerbet Branched Esters

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Liquidity of Product

Critical Considerations:

- Selection of the hydrophobe
- Number of carbon atoms present.
- Branching (Type and Location)
- Unsaturation

All effect liquidity & surface-active properties

What is the effect of branching on oil phases

- particularly esters?

Factors Effecting Liquidity

- Unsaturation
    - rancidity

- Branching
    - purity
    - consistency

Guerbet Branching

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

- Marcel Guerbet [1] first synthesized (1890s)
- Reaction sequence relates to Aldol Reaction
- Occurs at high temperatures, under catalytic conditions

Reaction Sequence[4]

1. The reaction takes place without catalyst, but it is strongly catalyzed by addition of hydrogen transfer catalysts.

2. At low temperatures 130-140 ^{o}C the rate-limiting step is the oxidation process (i.e. formation of the aldehyde).

3. At somewhat higher temperatures 160-180 ^{o}C the rate-limiting step is the Aldol Condensation.

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

Reactive Mechanism

- The product is an alcohol with twice the molecular weight of the reactant, minus a mole of water.
- The reaction proceeds sequentially：

  A) oxidation of alcohol to aldehyde.

  B) Aldol condensation after proton extraction.

  C) dehydration of the Aldol product.

  D) hydrogenation of the allylic aldehyde.

Guerbet Alcohols

High molecular weight, therefore:

- low irritation properties.
- branched, liquid to extremely low temperatures.
- low volatility
- primary alcohols -reactive and can be used to make many derivatives.
- useful as superfatting agents to re-oil the skin and hair.
- good lubricants.

Guerbet Alcohols

Essentially saturated, therefore:

- exhibit oxidative stability at elevated temperatures
- excellent color initially and at elevated temperatures
- exhibit improved stability over unsaturated products in many formulations.

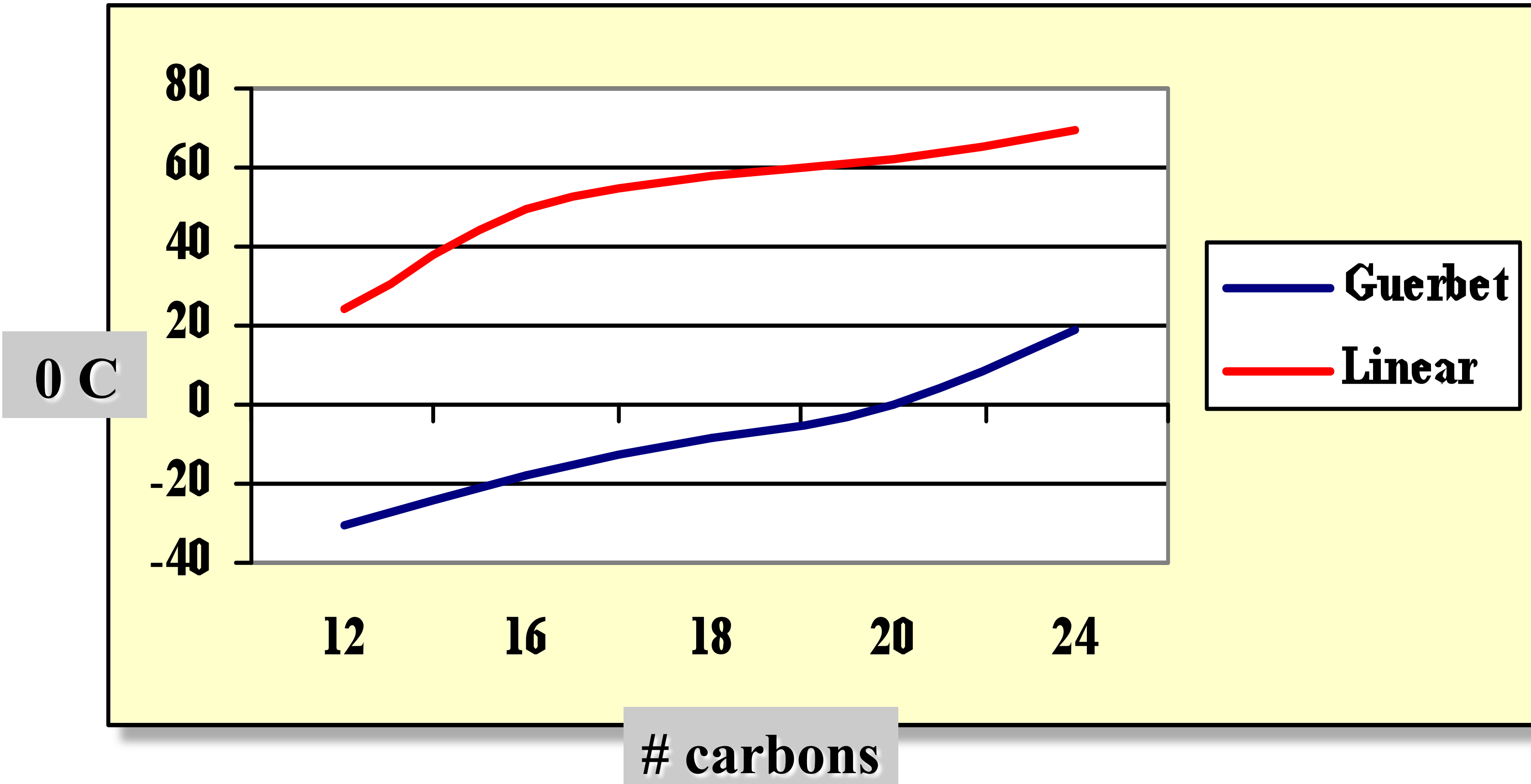
Melting Points

Various Alcohols

Carbon Number	Linear	Guerbet
12	24C	- 30C
16	50C	-18C
18	58C	-8C
20	62C	0C
24	69C	19C

Melting Points

guerbet vs linear alcohols



GUERBET ACIDS

Alcohol oxidation can be achieved by the dehydrogenation of the alcohol with alkali metal salts, called oxidative alkali fusion, which gives excellent yields of carboxylic acids.[6,7,8]

$$\underset{\textbf{Octyldodecanol}}{CH_3(CH_2)_9\overset{\overset{(CH_2)_7CH_3}{|}}{C}HCH_2\text{-}OH} \xrightarrow{NaOH} \underset{\textbf{Octyldodecanoic Acid}}{CH_3(CH_2)_7\overset{\overset{(CH_2)_7CH_3}{|}}{C}H\text{-}C(O)\text{-}OH} + 2\ H_2$$

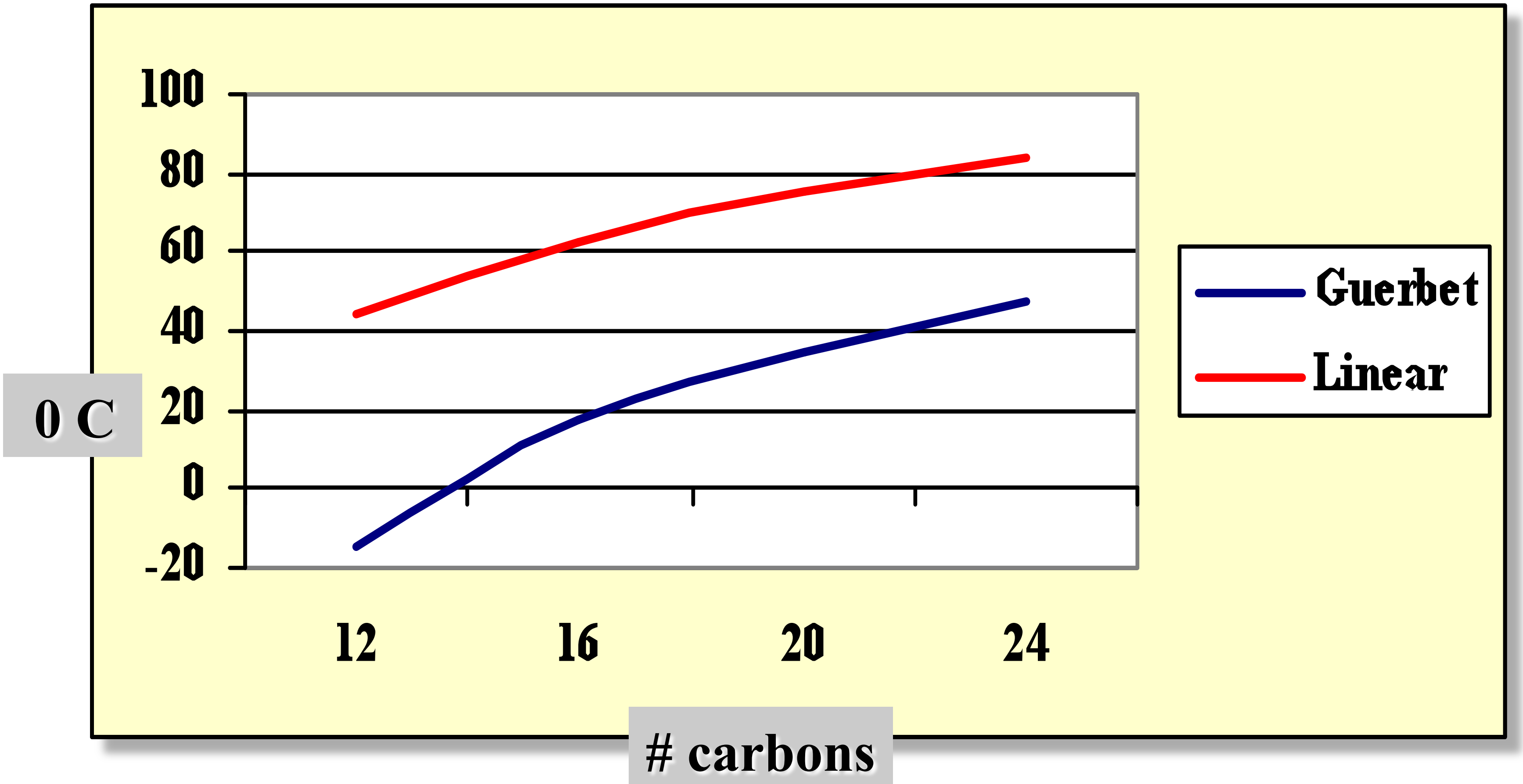
Melting Points

Various Acids

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

Melting Points

guerbet vs linear acids



Melting Points

Various Guerbet Compounds

Material	Guerbet Acid	Guerbet Alcohol
Hexyldecanoic (C16)	17 C	- 8 C
Octyldodecanoic (C20)	34 C	0 C

Titer Point

- The highest titer point ester was the one based upon both linear alcohol and linear acid.
- The incorporation of a guerbet branch in the alcohol portion of the molecule increased the titer point, resulting in an ester that is slushy below it's titer point, it was however pourable. The use of a guerbet acid and a linear alcohol resulted in a product that had a much lower titer point.
- The ester with the lowest titer point was made with both a guerbet alcohol and guerbet acid.

Ester Titer Point

Ester having 32 carbon atoms
16 in acid / 16 in alcohol

OH/Ac Type	Appearance	Titer Point
L/L	White Solid	34C
G/L	Slushy Liquid	50C
L/G	Yellow Liquid	9C
G/G	Yellow Liquid	< 0C

Ester Titer Point

Ester having 40 Carbon Atoms
20 in Acid / 20 in Alcohol

OH/Ac Type	Appearance	Titer Point
L/L	White Solid	38C
G/L	White Solid	48C
L/G	Yellow Liquid	34C
G/G	Yellow Liquid	< 0C

Class 1

Products having 32 Carbon Atoms

OH/Ac Designation	Type	Appearance	Titer Point
Cetyl Palmitate	L/L	White Solid	34 C
Hexyldecyl Palmitate	G/L	Slushy Liquid	50 C
Cetyl Hexyldecanonate	L/G	Yellow Liquid	9 C
Hexyldecyl hexyldecanonte	G/G	Yellow Liquid	< 0 C

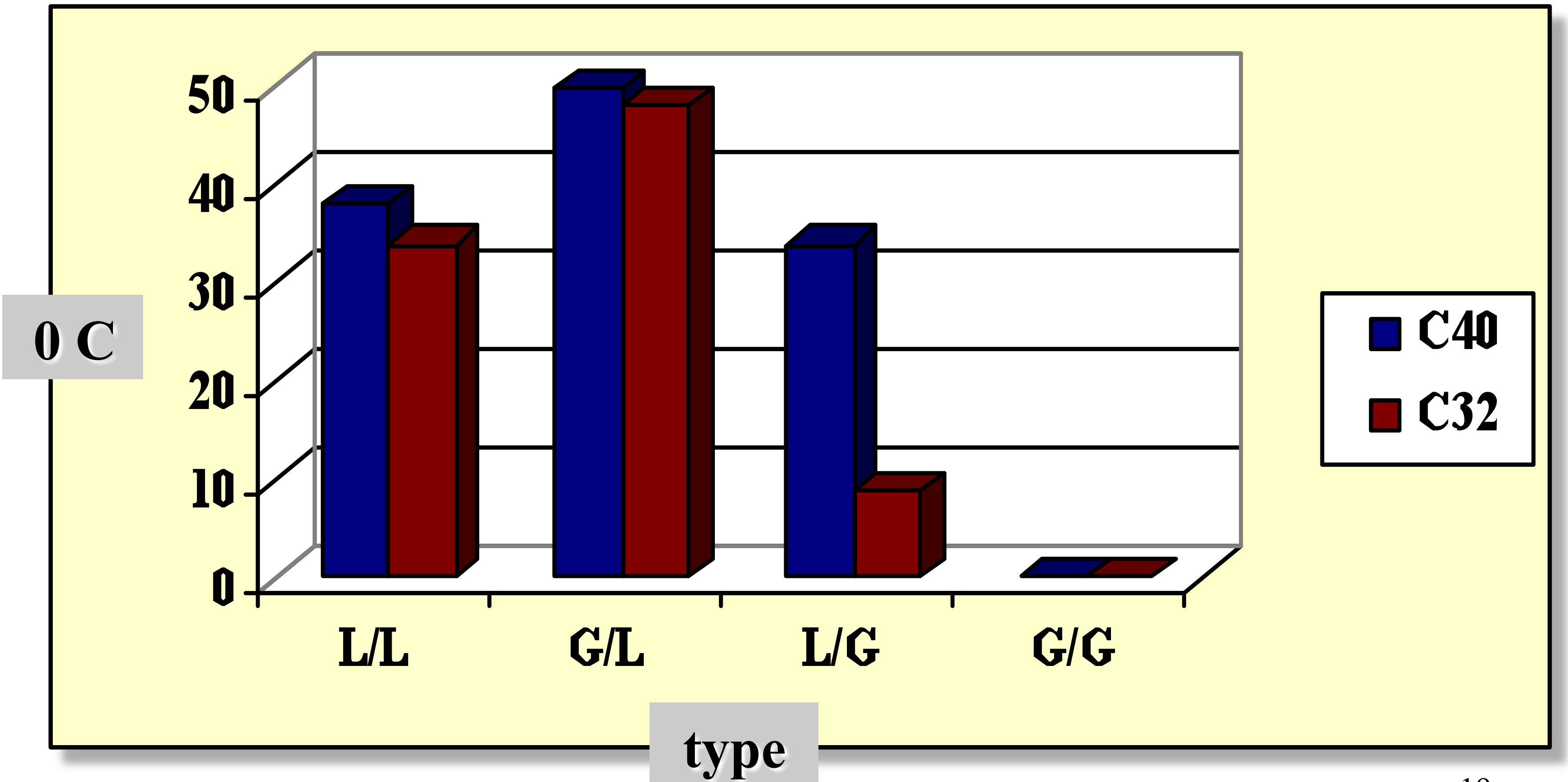
Class 2

Products having 40 Carbon Atoms

OH/Ac Designation	Type	Appearance	Titer Point
Eicosanoyl Eicosanate	L/L	White Solid	38 C
Octyldodecyl Eicosanate	G/L	White Solid	48 C
Eicosanoyl Octyldodecyonate	L/G	Yellow Liquid	34 C
Octyldodecyl Octyldodecyonate	G/G	Yellow Liquid	< 0 C

Ester Titer Points

compared by alcohol/acid type and number of carbon atoms



Ester Solvent Properties

OH/AC	Designation	Solvent Properties
Cetyl Palmitate	(L/L),C_{32}	1
Hexyldecyl Palmitate	(G/L),C_{32}	6
Cetyl Hexyldecanonate	(L/G),C_{32}	7
Hexyldecyl hexyldecanonte	(G/G),C_{32}	10
Eicosanoyl Eicosanate	(L/L),C_{40}	2
Octyldodecyl Eicosanate	(G/L),C_{40}	6
Eicosanoyl Octyldodecyonate	(L/G),C_{40}	7
Octyldodecyl Octyldodecyonate	(G/G),C_{40}	9
Control	no ester	0

Class 1

(products having 32 carbon atoms)

OH/AC Designation	Type	A	B	C	D	E
Cetyl Palmitate	(L/L)	I	S	S	I	S
Hexyldecyl Palmitate	(G/L)	I	S	S	I	S
Cetyl Hexyldecanonate	(L/G)	I	S	S	I	S
Hexyldecyl hexyldecanonte	(G/G)	I	S	S	I	S

Legend s = soluble i = insoluble

Solvent Designations:
A is water
B is isopropanol
C is cyclomethicone
D is dimethicone
E is mineral oil

Class 2

(products having 40 carbon atoms)

OH/AC Designation	Type	A	B	C	D	E
Eicosanoyl Eicosanate	(L/L)	I	S	S	I	S
Octyldodecyl Eicosanate	(G/L)	I	S	S	I	S
Eicosanoyl Octyldodecyonat	(L/G)	I	S	S	I	S
Octyldodecyl Octyldodecyonate	(G/G)	I	S	S	I	S

Legend s = soluble i = insoluble

Solvent Designations: A is water
B is isopropanol
C is cyclomethicone
D is dimethicone
E is mineral oil

Dry Times

32 carbon atoms esters

OH/AC

Designation	Type	Dry Time	Comments
Cetyl Palmitate	(L/L)	N/A	Solid
Hexyldecyl Palmitate	(G/L)	48 sec.	Slushy
Cetyl Hexyldecanonate	(L/G)	15 sec.	Liquid
Hexyldecyl hexyldecanonte	(G/G)	11 sec.	Liquid

Dry Times

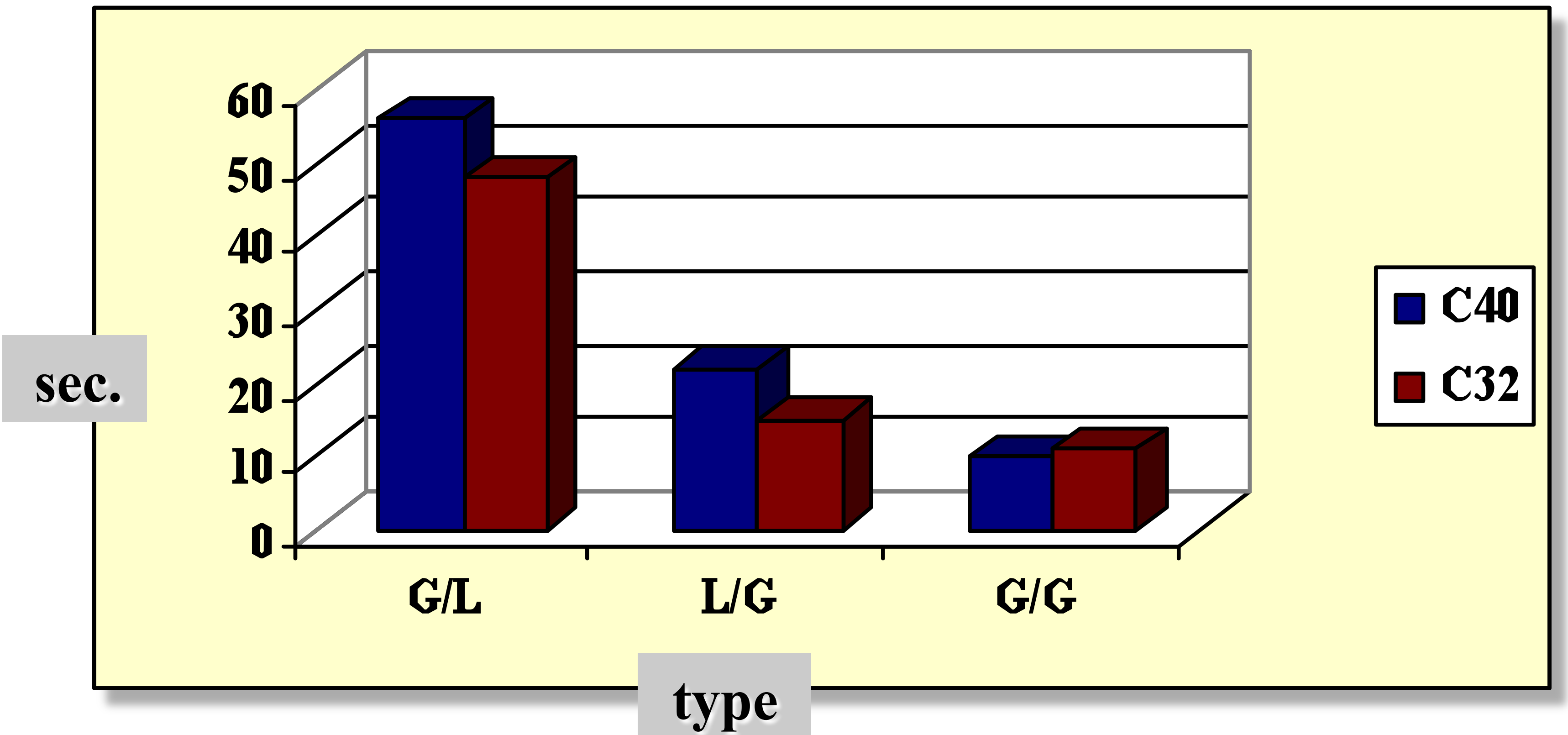
40 Carbon atom esters

OH/AC

Designation	**Type**	**Dry Time**	**Comments**
Eicosanoyl Eicosanate	(L/L)	N/A	Solid
Octyldodecyl Eicosanate Slushy	(G/L)	56 sec.	
Eicosanoyl Octyldodecyonate	(L/G)	22 sec.	Slushy
Octyldodecyl Octyldodecyonate	(G/G)	10 sec.	Liquid

Drying Time

Comparison on skin for esters with one or two guerbet components and 32 and 40 carbons



Physical Form

- The hardest most crystalline ester in each class was the one based upon both linear alcohol and linear acid. The incorporation of a guerbet branch in the alcohol portion of the molecule, while increasing the titer point, makes the ester slushy below it's titer point. The use of a guerbet acid and a linear alcohol resulted in a product which had a much lower titer point, but was slushy below it's titer point.

- Only the ester made with both a guerbet alcohol and guerbet acid remained liquid and clear below $0^{o}C$.