

Liquid Esters using Propoxylation Technology

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Abstract

Liquid esters are of interest in the formulation on many products. For example, the ability to control melting point is very useful in formulating skin care products. The options to make liquid products in the past were principally accomplished by incorporation of unsaturation or branching into the molecule. One particular branch type, the Guerbet branch is very effective for liquidity, but very expensive. A study was undertaken to determine the effects of using propylene oxide to improve liquidity of a series of esters.

A great deal of work has been done in recent times to prepare liquid esters that provide benefit to hair and skin. One very important benefit of such a product depending upon the exact structure is moisturization. Moisturization is the effect on the skin of blocking the loss of water. The mechanism is generally based upon the deposition of an oil on the skin that acts as a barrier to transepidermal water loss. In this case liquid esters are of interest since they can easily form a thin oily film on the skin. Esters based upon wax technology generally are neither effective nor have a desirable skin feel. There have been a number of approaches used to obtain liquid esters for use as moisturization agents.

One approach to getting functional liquid products has been the use of unsaturated hydrophobes. These materials include oleyl materials (C18 one unsaturation), linoleyl (C18 two unsaturation), eucalyptol products (C22 one unsaturation) and the like. This approach results in liquid products, but the products suffer from a process called rancidity. Rancidity is a process in which the double bonds present in the molecule is converted to an aldehyde, cleaving the double bond and producing an aldehyde that has half the molecular weight of the starting

unsaturated material. Unfortunately, these aldehydic compounds have a very bad smell and have been thought to be unacceptable in personal care product. The problem is likewise to occur in oils having unsaturation like soybean, rapeseed (also called HEAR oil) and olive oil. These oils have also been deemed unacceptable for personal care applications for rancidity considerations.

Materials having conjugated double bonds ($-C=C-C=C-$), are much more likely to oxidize than two double bonds that are distant from each other. The conjugated double bond is an order of magnitude more reactive than the simple double bond. This makes the conjugated double bond very undesirable vis-à-vis cosmetic products. What is very important to note is that the aldehyde resulting from the rancidity process in addition to having mal odor also can react with fragrances to destroy their effectiveness.

Recently, we have observed particular oil; meadowfoam oil that is very high in unsaturation is nonetheless very stable to oxidation. This oil, and the derivatives thereof, overcomes many of the problems associated with other oils. The material is both

intrinsically stable to oxidation due to the distance between the two double bonds, but also appears to possess a natural antioxidant that retards rancidity.

Meadowfoam Seed Oil (*Limnanthes alba*)

Meadowfoam oil is a triglyceride derived from the herbaceous winter plant (*Limnanthes Alba*). It is grown in the southern portion of the State of Oregon. Since the flowers have an appearance of a canopy of white foam, the name meadowfoam was given to the plant. This material is a relatively new raw material, and is unique in that it has both a high concentration of fractions at or above twenty carbons and it has a unique arrangement of double bonds. The fact that the double bonds in the doubly unsaturated product are not conjugated, as in linoleic acid, the oil is liquid to very low temperatures, and is stable to oxidation. Meadowfoam seed oil also has a natural antioxidant present, which improves oxidative stability.

Carbon Distribution

Component	Typical % Weight
C20:1(n=5)	63
C20:2 (=5,13)	12
C22:1 (n= 5)	3
C22:2 (n= 5, 13)	10

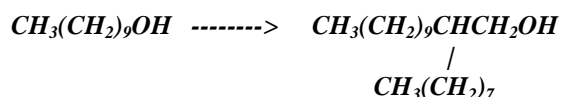
CAS Number: 153065-40-8
Iodine Value: 95

Another approach to obtaining liquid products is to introduce branching into the product. Specifically, short branching (including methyl ranching) can be introduced into a molecule as a consequence of the process used to make an alcohol. The oxo process for example introduces the methyl group into the molecule. Oxo alcohols are prepared by the reaction of alpha olefin with hydrogen and carbon monoxide

using a catalyst, commonly cobalt compounds. The reaction occurs in two parts, the first is the preparation of the aldehyde and the second is reduction of the aldehyde to the alcohol. What is very important is the fact that two different aldehyde compounds, one linear, the other with a methyl branch, form in the first part of the reaction. Both then rearrange into alcohols.

A particularly potent branch pattern that can be introduced is the guerbet branch. Guerbet Alcohols have been known since the 1890s when Marcel Guerbet first synthesized these materials¹. The reaction sequence that bears his name is related to the Aldol Reaction and occurs at high temperatures under catalytic conditions².

The overall Guerbet reaction can be represented by the following equation;



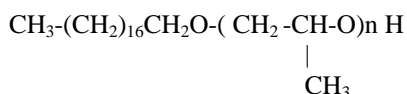
Whilst a very interesting process and if properly chosen, a very effective one in making liquid products, the guerbet products suffer from high costs.

This is due not only to the technical sophistication of the guerbet process, but also the high cost added to product by the various post process sequences used to refine and purify the product. These steps include, but are not limited to, distillation (to increase purity), hydrofinishing (to lower unsaturation), washing (to remove soap), and filtration (to remove catalyst).

There is therefore a need for a cost-effective method to obtain a series of products that are liquid and have a range of melting points for cosmetic and other applications. In order to address these needs, we

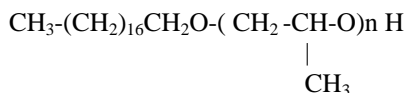
reacting the propoxylated alcohol with various fatty acids.

Propoxylation of Stearyl Alcohol



Experimental

Stearyl Alcohol was propoxylated to make the following compounds:



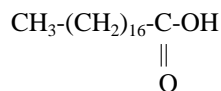
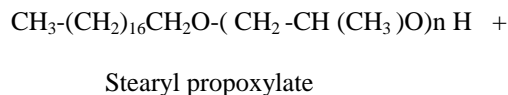
Designation	n value
O	0.0
A	0.7
B	1.5
C	2.2

Analysis Propoxylated Alcohol

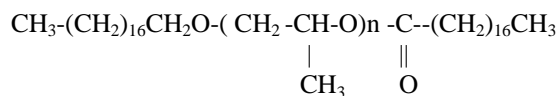
	O	A	B	C
Color (Gardner)	1	1	1	1
Appearance 50°C	Clear	Clear	Clear	Clear
pH 1% Aqueous	7.0	7.0	6.9	6.8
Acid Value	0.0	0.06	0.05	0.03
Hydroxyl Value	208.7	181.2	161.2	139.3
Moisture (%)	0.1	0.1	0.1	0.1
Titer point (°C)	49	38	31	27

C. Stearate Esters

The resulting propoxylated alcohols were then reacted with stearic acid using a tin catalyst.



Stearic Acid



Stearyl-ppg-stearate

Analysis propoxylated stearyl stearate

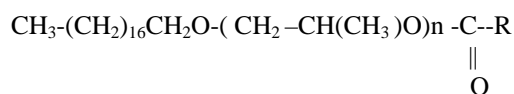
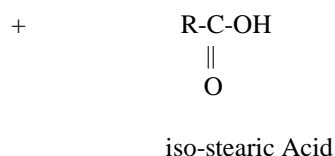
	S-O	S-A	S-B	S-C
Color (Gardner)	5	4	3	3
Appearance 50°C	Clear	Clear	Clear	Clear
Acid Value	2.0	3.1	2.9	3.8
Hydroxyl Value	7.6	6.8	8.0	7.0
Saponification Value	104.5	97.2	89.7	84.0
Titer point (°C)	51	41	38	29

iso-Stearate Esters

The resulting propoxylates were then reacted with stearic acid using a tin catalyst.



Stearyl propoxylate



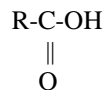
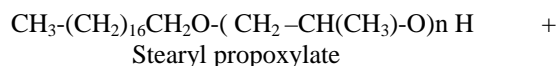
Stearyl-ppg-iso-stearate

Analysis propoxylated stearyl iso-stearate

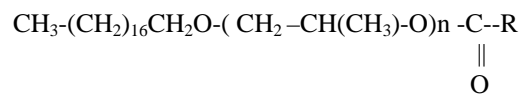
	i-S-O	i-S-A	i-S-B	i-S-C
Color (Gardner)	4	4	3	3
Appearance 50°C	clear	clear	clear	clear
Acid Value	3.0	4.1	3.7	2.8
Hydroxyl Value	7.9	8.2	7.7	6.8
Saponification Value	104.8	98.3	89.9	85.0
Titer point (°C)	26	20	15	12

2-Ethyl Hexanoic Esters

The resulting propoxylated products were then reacted with stearic acid using a tin catalyst.



2 ethyl hexanoic acid



Stearyl-ppg-2 ethyl hexanoate

Analysis Propoxylated stearyl 2-ethyl hexanoate

	2EH-O	2EH-A	2EH-B	2EH-C
Color (Gardner)	4	4	3	3
Appearance 50°C	clear	clear	clear	clear
Acid Value	2.6	3.2	4.1	3.8
Hydroxyl Value	7.6	7.2	6.4	7.7
Saponification Value	141.3	129.0	116.0	106.7
Titer point (°C)	41	31	29	27

D. Discussions and Conclusions

1. The propoxylation of stearyl alcohol prior to esterification results in the lowering of melting point for all the compounds studied. This confirmed the effect of branching upon melting point. Melting points of the alcohol were dropped by over 20°C by adding 2.2 moles of propylene oxide to the stearyl alcohol. Likewise significant melting point reductions were encountered when esters were evaluated.
2. The current study added up to 2.2 moles of propylene oxide to the hydrophobe. The melting

point of the propoxylate and of all derived esters were still dropping at the 2.2 mole level (relative to the lower levels). This was a surprise, since it was felt that at the 2.2 mole level the effectiveness of the oxide on liquidity would begin to drop essentially to zero. It is interesting to note that at 2.2 moles the percentage of propylene oxide added is 32.4% by weight.

3. It was likewise a surprise that the esterification of the stearyl propoxylate resulted in only a very modest increase in melting point, relative to the starting alcohol propoxylate. A very significant increase in molecular weight occurred, but a marginal change in melting point was noticed.
4. The 2 ethyl hexyl esters were less efficient in lowering the melting point of the resulting esters than were the isostearate. This was a surprise, since the 2-ethyl hexanoic acid is both lower molecular weight (C8) and more branched than the C-18 branched iso-stearate. The

propoxylated stearyl alcohol isostearate compounds had the lowest melting point of any of the homologous series studied.

5. We believe that the reaction of fatty alcohols with propylene oxide, then subsequent derivization will allow for the synthesis of a new class of compounds with very desirable properties on the skin. ‘

References

1. M. Guerbet, C.R. Acad. Sci. Paris, 128, 511; 1002 (1899)
2. O'Lenick, Jr. Anthony J. and Bilbo, Raymond E., Guerbet Alcohols, Versatile Hydrophobes, SCCS, April, 1987.
3. Morrison, Robert and Boyd, Robert, Organic Chemistry, 3rd Edition, (1973) p. 582.

Anthony J. O'Lenick, Jr. is President of Siltech LLC. in Dacula, Ga., a silicone and surfactant specialty company. Prior to that he held technical and executive positions at Alkaril Chemicals Inc, Henkel Corporation and Mona Industries. He is a fellow in the American Institute of Chemists. He has published over 30 technical articles in trade journals, written a book on surfactants, contributed chapters to three books, and is the inventor on over 180 patents. In addition, He received a number of awards for work in silicone chemistry including the 1996 Samuel Rosen Award given by the American Oil Chemists' Society, the 1997 Innovative Use of Fatty Acids Award given by the Soap and Detergents Association, and the Partnership to The Personal Care Award given by the Advanced Technology Group.