REVIEW ARTICLE

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PALM DIHYDROXYSTEARIC ACID (DHSA): A MULTIFUNCTIONAL INGREDIENT FOR VARIOUS APPLICATIONS

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ABSTRACT

Palm dihydroxystearic acid (DHSA) is derived by catalytic reaction from palm oil-based or palm kernel oil-based oleic acid, vegetal renewable sources of many interesting ingredients. Once crystallised, the product is off-white in colour, tasteless with a slight acid smell and is non-irritant to the skin. The DHSA structure is peculiar as it contains a carboxyl group and two hydroxyl groups at the 9 and 10 positions of the C18 carbon chain. Such structure leads to many interesting applications. When used in cosmetics, it significantly changes the properties of oily phases and wax gels. It can also interact strongly with the solid surfaces of pigments and inorganic fillers, leading to better colour development, long lasting skin adhesion- and better pay-off properties. Such a combination of properties and effects lead to many interesting applications particularly for cosmetics. As an additive in a transparent soap formulation, DHSA has been found to enhance the transparency of the soap. Besides, DHSA is also a potential feedstock for various derivatives through substitution reactions onto one, two or all three reactive sites. Some alkyl esters from DHSA have been studied, which show exceptional skin feel and powder binding capability. Metallic soaps of DHSA have shown pigment coating capability and a set of different properties when compared to the usual metallic stearates. Many more derivatives such as monoglycerides, estolides, alkanoamides, have been derived from DHSA to exploit all the possible derivatisation potential of DHSA. Hence, the aim of this article is to review all the works on palm DHSA that have been done so far in the Malaysian Palm Oil Board (MPOB) under the purview of the value addition strategy.

Keywords: dihydroxystearic acid, oleic acid, derivatives, multifunctional ingredient.

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INTRODUCTION

A consistent and predictable supply of palm kernel oil (PKO) and palm oil (PO) has led to the development of oleochemical industry in Malaysia. The industry, which started in 1980s, is now one of the largest oleochemical complexes in the world, with the production capacity of about 2.6 million tonnes, representing about 20% of the world's capacity. In this respect, the oleochemical industry is contributing significant additional revenue over the basic value of the commodity oils for Malaysia. In 2013, the export of oleochemical products rose by 4.8% to 2.73 million tonnes from 2.60 million tonnes in 2012 (MPOB, 2013).

However, Malaysia's palm oil non-food downstream segment is mainly focused on basic oleochemical products: fatty acids, fatty alcohols, methyl esters and glycerin. These basic oleochemicals constitute 99% of the palm oil non-

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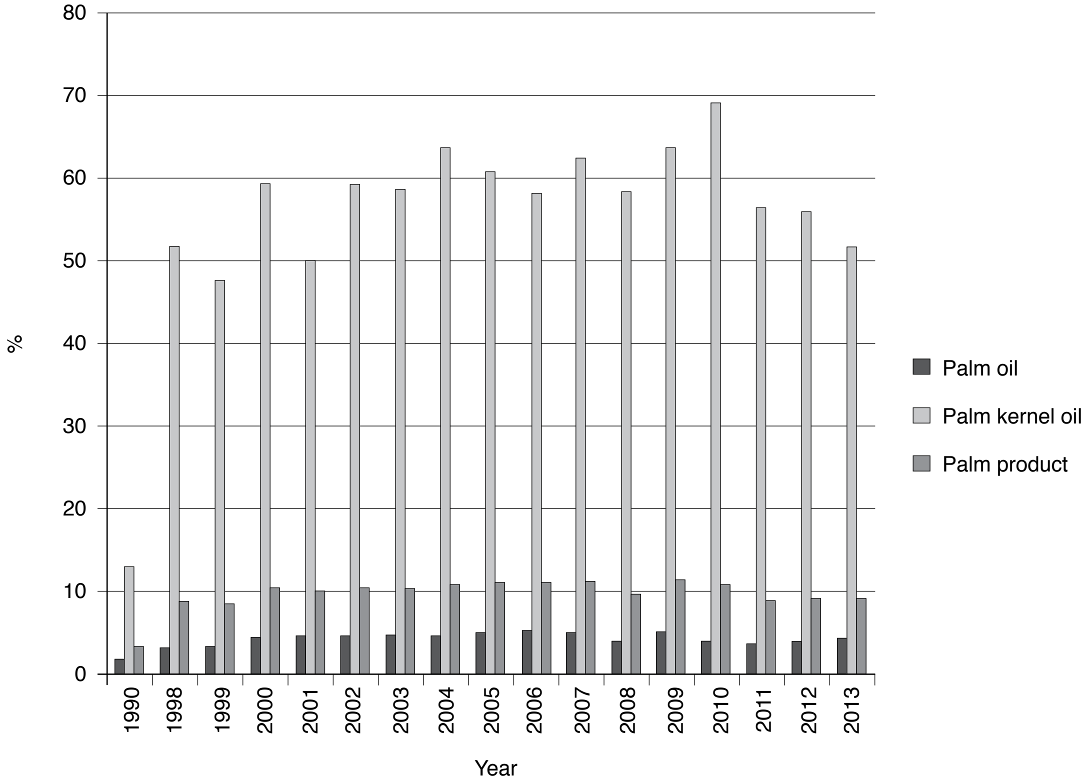
food downstream production, while the remaining 1% is contributed by oleo derivatives that are developed from basic oleochemicals and used in consumer products like soaps, detergents and cosmetics. The capacity for two basic oleochemicals, *i.e.* fatty acids and fatty alcohols, is much higher than global demand. The issue is further compounded by the fact that these have lower profit margins (7% on average) compared to the high-value oleo derivatives (20% on average).

The Malaysian oleochemical industry has been consuming about 60% of PKO and only about 5% of PO as feedstock as shown in *Figure 1*. Overall, the total utilisation of palm products (PP) as feedstocks for the oleochemical industry is only about 10%. Hence, there is abundance of raw materials available for the downstream activities in Malaysia.

The use of lauryl-myristyl alcohols for the production of alkyl sulphates as active ingredients for cleaning purposes, is a well-established industry, which has created a demand for lauric oils. The major lauric oils traded in the world market are coconut oil and PKO, with PKO being the major oil. Besides lauric (C12) and myristic (C14), PKO also contains other fatty acids including caproic (C6), caprylic (C8), capric (C10), palmitic (C16), stearic (C18) and oleic (C18:1) acids. If the demand is for lauric and myristic acids, the oleochemical industry in Malaysia usually split the oil, whereby the fatty acids of C10 and below are removed (stripped) and the C12-C14 are distilled off leaving a by-product which contains C16, C18 and C18:1 fatty acids. The by-product is usually fractionated to yield C16-C18 and C18:1 fractions. These fractions fetch lower prices compared to the C12-C14 fraction. With the increase in production of C12-C14 fraction, the production of fractions of low commercial value also increases. This article will review and highlight the use of oleic acid (C18:1) fraction, the by-product of the oleochemical industry as feedstock for a new derivative of dihydroxystearic acid (DHSA). This review is intended to enlighten the industry on the potential value addition of the new derivative, DHSA, as a multifunctional ingredient for various applications.

DIHYDROXYSTEARIC ACID (DHSA)

Between the two low value fractions of the by-products of the oleochemical industry, which contain C18:1 and C16-18, the former or the crude oleic acid fraction offers interesting possibilities since it contains a degree of unsaturation and therefore a potential for further chemical modification. One possible chemical modification is converting the unsaturation to an epoxide via peracetic acid or performic acid routes, followed by hydrolysis to yield 9,10-dihydroxystearic acid (*Figure 2*) or in short DHSA (Ahmad *et al*., 2004; 2009; Awang and Ahmad, 2001; Awang *et al*., 1998; 2001a; 2002; Siwayanan *et al*., 2004; 2005).



Source: MPOB (2013a).

Figure 1. Percent utilisation of palm products (PP) in the Malaysian oleochemical industry.

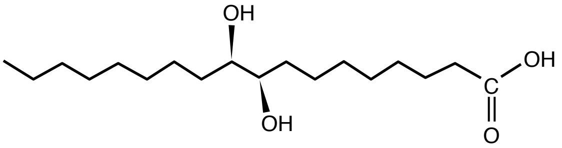


Figure 2. The 9, 10-dihydroxystearic acid (DHSA).

This fatty acid exhibits a characteristic structure as it contains, besides the reactive carboxylic group, two vicinal alcohol groups. It is fairly hydrophilic when compared to stearic acid and it behaves like a long-chain fatty acid and is able to determine physico-chemical bonds with polar surfaces. Such structure leads to many interesting applications. In cosmetics, it changes the properties of oily phases and wax gels significantly. Moreover, it interacts strongly with the solid surfaces of pigments and inorganic fillers, leading to better colour development, long-lasting skin adhesion- and better pay-off. Contrary to many traditional molecules, the polarity of DHSA is at two molecular sites, thus providing unusual behaviour to micronised suspensions. Indeed, even if water-insoluble, it crystallises with one water molecule, suggesting strong polar interactions with polar sites of other molecules and surfaces. Full development works have been applied to its properties in make-up products and emulsions (Rigano, 2003; Ismail *et al.*, 2004; 2006b, c; 2008; 2009).

It is also interesting to note that many derivatives can also be formed from DHSA through substitution reactions onto one, two or all of the three reactive sites. Some alkyl esters have also been studied (Awang and Ahmad, 2000; 2003; Awang *et al.*; 2000; 2003; 2004a, b; 2005a; 2007a; Chua *et al.*; 2006; 2007) which show exceptional skin feel and powder-binding capability. The DHSA derived metallic soaps have also been prepared, that show pigment coating capability and a set of different properties when compared to the usual metallic stearates. The DHSA itself can work as a pigment coating ingredient.

The DHSA and derivatives can be used in a variety of applications for example as corrosion inhibitors, gemini surfactants, cosmetic ingredients and many more. Its application as a cosmetic ingredient was found to be interesting and provided an avenue to add value to a low value product such as the technical grade oleic acid used for its preparation (Ahmad *et al.*, 2008a, b; 2009; Awang *et al.*, 2001b; Awang, 2008; Ismail *et al.*, 2004; 2008; 2009).

Production of DHSA

The DHSA was initially produced by MPOB at laboratory scale using C18:1 fraction of palm-based oleic acid, commercially available from oleochemical producers in Malaysia. The commercial oleic acid, which has the purity in the range of 71.4%–78.0%, is a low value by-product produced during the extraction of lauric (C12) and myristic (C14) acids from PKO and palmitic (C16) acid from PO. The C18:1 fraction contains the unsaturation needed for epoxidation and hydrolysis processes for the production of DHSA. The laboratory process to produce DHSA from oleic acid has been filed for intellectual property right in Malaysia and Singapore (Awang *et al*., 1998; 2002).

The peracetic acid (PAA) route was scaled up from laboratory to the pilot plant scale (500 kg per batch). In this process route, as shown in *Figure 3*, the PAA was pre-formed *in situ* by reacting the glacial acetic acid (>99%) and hydrogen peroxide (50%) in the presence of sulphuric acid. This PAA, which acted as an oxidising agent, spontaneously converted the unsaturation present in the oleic acid (73.6%) to form the epoxides. Both the epoxidation and hydrolysis processes were carried out in the reactor (R2). The crude DHSA was washed for five to six times with hot water in the settler (S1) to remove the remaining acid present in the crude DHSA. The washed crude DHSA contains 55%-58% DHSA (Siwayanan *et al*., 2004; 2005).

The process of converting oleic acid into DHSA was further simplified and improved via performic acid (PFA) route as shown in *Figure 4* (Siwayanan *et al*., 2004; 2005; Ahmad *et al*., 2004; 2009). The main reactions involved in this PFA route include the reaction between formic acid (94%) and hydrogen peroxide (50%) in the presence of sulphuric acid as a catalyst (98%) to form performic acid, followed by the reaction between *in situ* formed performic acid with the unsaturation present in the oleic acid (70%-78%) to form the epoxides and finally the hydrolysis of the epoxides to form DHSA. All reactions occurred in the reactor R2. The production cost and the yield of crude DHSA based on the two different routes are shown in *Table 1*.

Purification of Crude DHSA

The crude DHSA was purified by three processes: (i) recrystallisation from solvent, (ii) solvent removal, and (iii) drying process. The purification process is required to remove acids present in the crude DHSA, which can cause skin irritation. Higher yield of purified DHSA was obtained via the crystallisation process using isopropanol/water mixtures of 80:20 (v/v) ratio and 1:1 (w/v) ratio of crude DHSA. The crude DHSA, while hot (at 60°C) was mixed with the isopropanol/water in a drum of 120-litre capacity and this mixture was cooled at 5°C for the crystallisation to take place. The DHSA crystals (in wetted cake form) were then transferred to a mechanical vibrating screen to separate the solvent from the DHSA crystals. A piece of cloth having fine pore size was placed on

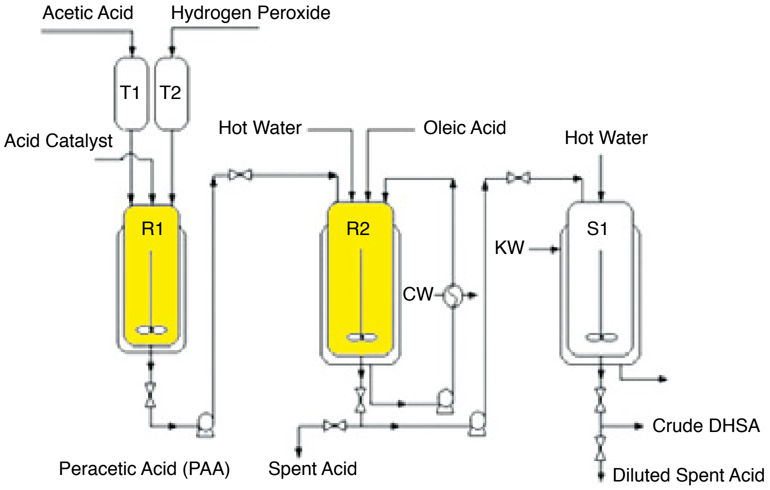


Figure 3. Process flow diagram of peracetic acid (PAA) route.

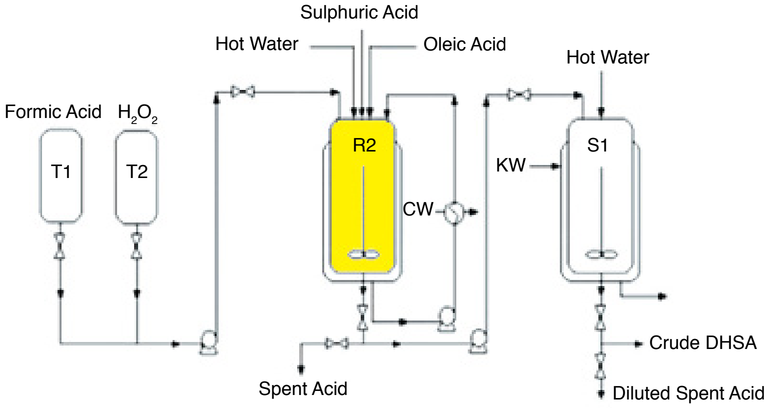


Figure 4. Simplified process flow diagram of performic acid (PFA) route.

TABLE 1. COMPARISON OF 9, 10 DIHYDROXYSTEARIC ACID (DHSA) PRODUCTION VIA PERACETIC AND PERFORMIC ACID ROUTES

Parameters	Peracetic acid route	Performic acid route
Production yield (%)	72.5	96
Production cost	Reference	30% cheaper
Batch processing time (hr)	12	10
No. of reactor required	Two, R1 and R2	One, R2

the top surface of the screen in order to prevent the fine DHSA crystals from passing through the cloth. After removal of isopropanol through the vibrating screen, the purified DHSA was washed with water. The washed purified DHSA was then dried under the sunlight for two to three days (Siwayanan *et al.*, 2005). The typical specification of purified DHSA is shown in *Table 2*.

Various solvents and effects of parameters such as temperature, concentration, ratio and cooling mode were also studied (Siwayanan *et al.*, 2004; 2005; Koay *et al.*, 2006; 2007; 2009; 2011b; 2012; Sumaiya *et al.*, 2007; 2010; Zainal-Abidin *et al.*, 2009) for the crystallisation or washing purposes. A summary of these effects is shown in *Table 3*.

Safety Evaluation of Palm DHSA

As a potential new ingredient for consumer products, the safety of DHSA is therefore very important. The irritation potential of DHSA to the eye and skin was assessed using *in vitro* ocular and dermal irritection assays and confirmed by *in vivo* patch test. Its potential in inducing sensitisation was confirmed by the *in vivo* human repeated insult patch test (HRIPT). *In vitro* studies showed no ocular or dermal irritation potential in using purified DHSA while *in vivo* studies showed that the purified DHSA did not induce any significant cutaneous skin irritation, cumulative skin irritation or sensitisation at 1%, 3% and 5%, respectively (Zafarizal *et al.*, 2005).

TABLE 2. SPECIFICATIONS OF CRUDE AND PURIFIED DIHYDROXYSTEARIC ACID (DHSA)

Specifications	Crude DHSA	Purified DHSA
DHSA purity (%)	56.6-58.0	70.9-79.9
Water content (%)	5.2	1.1-1.3
OHV (mg KOH g^{-1})	220.7	291.5-357.6
Iodine value (g I_2/100 g)	7.3-9.1	2.9-4.0
Acid value (mg KOH g^{-1})	160.6	172.7
Melting point (°C)	79.4-79.8	89.8-90.3
Irritancy	Irritant	Non-irritant
Form/particle size (micron)	Semi-solid	40-120

TABLE 3. EFFECTS OF VARIOUS PARAMETERS ON DIHYDROXYSTEARIC ACID (DHSA) PURIFICATION

Parameters	Siwayanan *et al.* (2004)	Koey *et al.* (2006)	Sumaiya *et al.* (2007)	Koey *et al.* (2009)	Abidin *et al.* (2009)	Sumaiya *et al.* (2010)
Crystallisation type	Solvent crystallisation	Solvent crystallisation	Solvent crystallisation	Solvent crystallisation	Solvent crystallisation	Solvent crystallisation
Solvent type	IPA	IPA	Ethanol	Ethanol & IPA	Ethanol	Ethanol
No. of purification stages	Two	One	One	One	One	One
Solvent concentration	80%	60%-100%	Not specified	90%-100%	Not specified	90%-100%
Solvent ratio crude DHSA	Not specified crude DHSA	100%-150%	100%-200% DHSA	Not specified	100% crude	100%-200% crude
Crystallisation period	Not specified	12 hr	24 hr	24 hr	12 hr	24 hr
Starting temperature	60°C	80°C	Not specified	80°C	65°C	80°C
Final temperature	5°C	RT	RT	20°C	24°C-28°C	20°C
Cooling rate	Uncontrolled	Uncontrolled	Uncontrolled	0.2°C-0.8°C min^{-1}	0.6°C min^{-1}	0.8°C min^{-1}
Crystalliser type	Freezer at 5°C	Conditioned room without convective air flow	Conditioned room without convective air flow; freezer at 5°C	Custom fabricated simultaneous batch crystallisation unit	Custom fabricated simultaneous batch crystallisation unit; conditioned room without convective air flow	Custom fabricated simultaneous batch crystallisation unit; conditioned room without convective air flow
Mode of solvent removal	Mechanical vibrating screen	Vacuum filtration	Vacuum filtration	Vacuum filtration	Vacuum filtration	Vacuum filtration
Water washing	Required	Not required	Not required	Not required	Not required	Not required
Mode of crystal drying	Not specified	Mechanical induced ventilation at RT for 48 hr	Oven dried at 50°C for 48 hr drying	Oven dried at 50°C for 48 hr	Oven dried at 50°C for 48 hr	Oven dried at 50°C for 48 hr
Purity of crude DHSA	56.6%-58%	69%	Not specified	68.5%	Not specified	Not specified
Purity of DHSA crystals	70.9% (1st stage) 79.9% (2nd stage)	86.6%-92.2%	86.8%-91.4%	80.2%-93.0%	88.2%-94.7%	73.3%-91.4%

Source: Koay *et al.* (2011a).

APPLICATIONS OF DHSA

Sodium DHSA Soap

The sodium soap of DHSA was prepared by reacting DHSA and sodium hydroxide (NaOH). The DHSA (50 g) was placed in a reaction flask, and depending on the mole ratio, a sufficient amount of 50% NaOH solution was added in 5 ml portions with continuous stirring. When the addition of NaOH was completed, the mixture was stirred for a further 45 min at 70°C-75°C. The product obtained was dried to a constant weight in an oven at 80°C (Awang *et al*., 2001b).

The soap properties, such as foamability, detergency, biodegradability and wetting power were evaluated. The foaming properties of DHSA soap was examined by pouring the surfactant solution (0.1%) into a 500 ml measuring cylinder and foam was whipped up with 30 vigorous strokes of a perforated plunger. While the detergency of soap solutions containing 50 ppm, 150 ppm and 350 ppm $CaCO_3$ at room temperature on soil cloth, AS9, was determined by a Terg-o-tometer. The DHSA soap had higher foamability and detergency than stearic acid soap, and comparable to palm stearin sulphonated methyl ester (SME) at room temperature. The DHSA soap degraded more than 60% in 28 days, but stearic acid soap only 30%. The wetting time for DHSA soap was 2 min, comparable to SME but faster than stearic acid soap. DHSA soap also exhibited good corrosion inhibition with a corrosion rate of 0.002 mm yr^{-1} at 100 ppm (Awang, *et al*., 2001b).

DHSA as a Transparency Enhancer in Transparent Soap Formulation

Palm DHSA has been found to be able to increase the transparency of soap (Ahmad *et al*., 2008a, b; 2009). DHSA is mixed with other ingredients as shown in the basic formulation of transparent soap (*Table 4*). The ingredients are mixed in jacketed stainless steel vessel, where they are melted to give a clear solution. The soap solution is poured into a mould and is then cooled to give a transparent soap.

TABLE 4. FORMULATION OF A BASIC TRANSPARENT SOAP

Ingredients	Composition (%)
Stearic acid	5-30
Myristic acid	5-30
Triethanolamine (TEA)	0.1-30
Sodium hydroxide (NaOH)	0.1-10
Ethylenediaminetetra-acetic acid (EDTA)	0.1-5
Sodium sulphite (Na_2SO_3)	0.1-5
Water	5-40
Sucrose	0.5-10
Glycerin	2-35
Surfactant	1-10
Ethanol	1-10
Lactic acid	1-5

Properties of Palm-based Transparent Soap with DHSA

Transparency. Transparency is the most important parameter in order to produce a good transparent soap. It is measured using Transparency meter which is based on light scattering effect of a laser light that passes through a slice of 1 cm thick soap. The transmission of a standard glass is 1.00 and this value is regarded as the highest transparency index value. The result as shown in *Figure 5* illustrates the transparency index of soap using fatty acids only (STD1) as a control, soaps made from combination of fatty acids with 1%, 3% and 5% of crude DHSA, purified DHSA and hydroxystearic acid (12-HSA), and a commercial soap (Comm 1). Analysis of variance indicated that soaps with 1%, 3% and 5% of crude DHSA and purified DHSA are more transparent than Comm 1 and STD1. Therefore, the transparency of the soap is improved by adding crude DHSA or purified DHSA. However, there is no significant difference between soaps with 3% and 5% of crude DHSA. In addition, soaps with 1% and 3% of purified DHSA also showed no significant difference.

Cleaning power. *Figure 6* shows the cleaning power of soap using fatty acids only (STD1) as a control, soaps made from combination of fatty acids with 1%, 3% and 5% of crude DHSA, purified DHSA and 12-HSA and a commercial soap Comm 1 in 50 ppm, 150 ppm and 350 ppm of water hardness. The results showed that the cleaning power of soaps with 1%, 3% and 5% of purified DHSA was higher than soaps with crude DHSA, 12-HSA, Comm 1 and STD1 in 50 ppm, 150 ppm and 350 ppm of water hardness. The addition of 12-HSA in the soap decreased the cleaning power of the soaps.

Foaming power and foam stability. A good soap should exhibit high foaming power and maintain foam stability. *Figure 7* shows the foaming power and foam stability of the soap made from fatty acids only (STD1) as a control, soaps made from combination of fatty acids with 1%, 3% and 5% of crude DHSA, purified DHSA and 12-HSA in 50 ppm, 150 ppm and 350 ppm of water hardness. The foaming power and foam stability of soaps with 1%, 3% and 5% of crude DHSA and purified DHSA are higher than Comm 1,

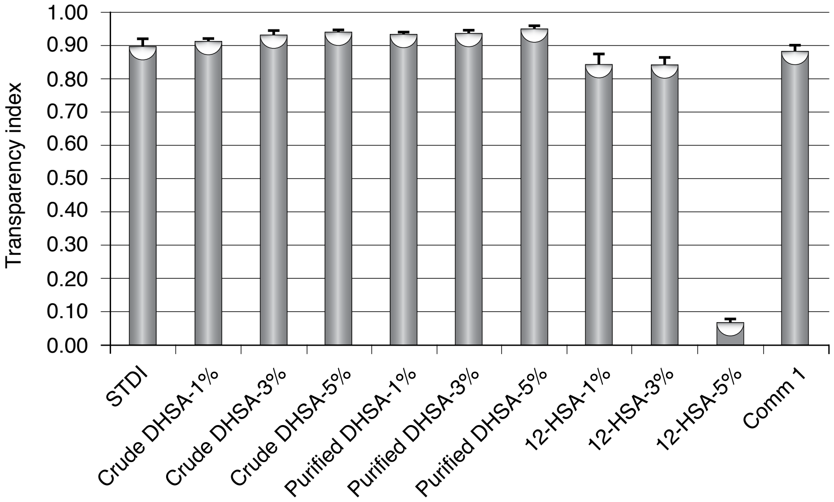


Figure 5. Transparency index of soap using fatty acids only (STD1) as a control, soaps made with combination of fatty acids with 1%, 3% and 5% of crude dihydroxystearic acid (DHSA), purified DHSA and 12-HSA and a commercial soap (Comm 1).

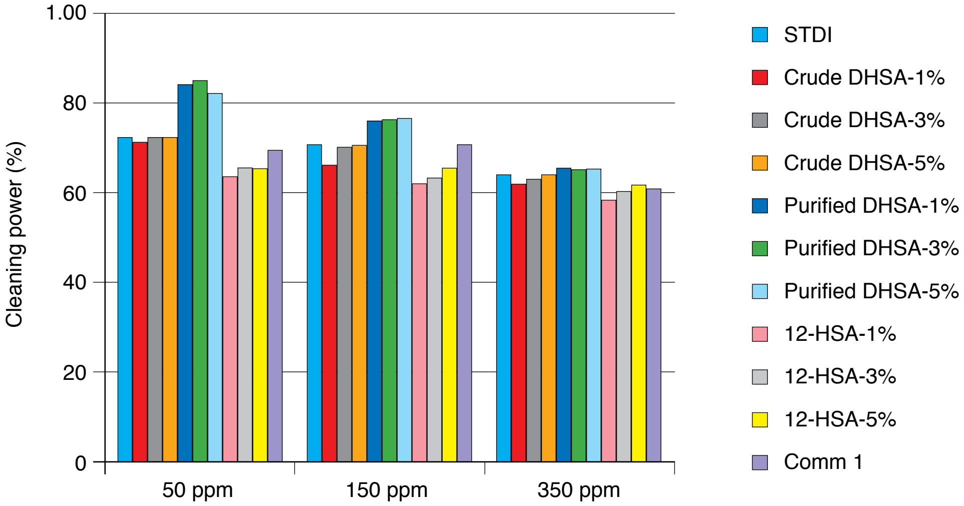


Figure 6. Cleaning power of soap using fatty acids only (STD1) as a control, soaps made with combination of fatty acids with 1%, 3% and 5% of crude dihydroxystearic acid (DHSA), purified DHSA and 12-HSA and a commercial soap Comm 1 in 50 ppm, 150 ppm and 350 ppm of water hardness.

but are comparable with STD1 in all water hardness. However, by adding 12-HSA in the soap, foaming power and foam stability decreased compared to those soaps with crude DHSA and purified DHSA.

Therefore, it can be concluded that by adding DHSA into transparent soap formulations, the transparency of the soaps is enhanced compared to soaps with ordinary transparency agents.

DHSA IN COSMETIC AND PERSONAL CARE APPLICATION

Pigment Coating with DHSA

It is possible to obtain hydrophobic stable pigments, by precipitation or physical coating techniques. In the case of physical coating, DHSA is dissolved in alcohols or acetone at 70°C. The solution is blended with pigments (at a ratio of DHSA/pigments equal to 10% w/w) then the solvent is evaporated to dryness while mixing. The coated pigment can also be prepared using salts of divalent metals such as zinc, calcium, magnesium and trivalent metal aluminium. Aqueous solutions of the chlorides of these metals are used to pre-treat the pigment before an alkaline solution of DHSA is added. Metallic DHSA salt precipitates on the pigment surface and modify its characteristic.

The use of pigments coated with DHSA can increase the characteristics of spreading and shine of finished products. DHSA works by reducing the adsorption and absorption power of powders and as coating and dispersing agent for pigment (Rigano, 2003; Ismail *et al*., 2004; 2006b, c; 2008; 2009).

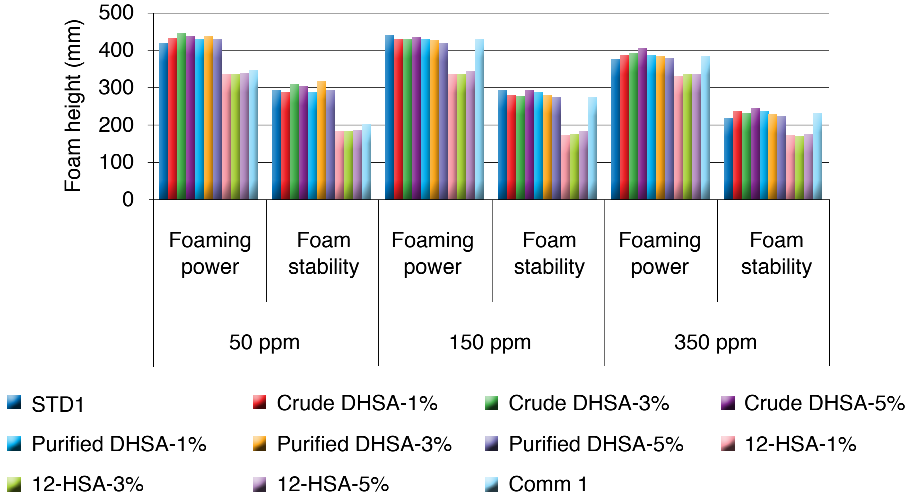


Figure 7. Foaming power and foam stability of soap using fatty acids only (STD1) as a control, soaps made with combination of fatty acids with 1%, 3% and 5% of crude dihydroxystearic acid (DHSA), purified DHSA and 12-HSA and a commercial soap (Comm 1) in 50 ppm, 150 ppm and 350 ppm of water hardness.

Pigmented Formulations

The DHSA and DHSA-coated pigments have been used in lipstick, lip gloss, mascara and blusher formulations as a thickening agent for oils and fats, a binder in compact powders and a strengthener, a spreading agent and shine aids in lipsticks. The DHSA-coated pigments may also influence the skin moisturisation.

Lipsticks

Physical DHSA-coated pigments improve shine and long-lasting characteristics of the sticks. When DHSA is used in the wax phase, it improves pay-off and application easiness, and the strength of the stick is also increased. The zinc salt, used as pigment coating, eliminates the 'motor-boat (oil strips left behind after application)' effect, as it gives a better coordination of the oils in the wax phase.

Gloss

In lip glosses, Zn-DHSA coated pigments noticeably improve pay-off and trace homogeneity.

Make-up Emulsions with DHSA

In make-up, emulsions, also known as the vehicle, are now more important than pigments, both in terms of formulation complexity and for the standard types of pigment used in the mascaras and the foundations. Moreover, the amount of pigment in the formula is low (8%-10%). Water is used both as the emulsion phase and as the evaporating ingredient, in order to make easy and adjust the mistakes of the application phase. Controlled evaporation, easy spreading, sweat and tears fastness, elasticity and film forming properties are key issues. In make-up products that require highly qualified spreading performance, a remarkable contribution to application and homogeneity of results is given by a special type of coating as described above. An example of eye mascara formulation, as shown in *Table 5*, makes the eye lashes look thicker and longer. The prepared mascara can also curl the eye lashes efficiently and effectively without stiffening them. The surface of the granules is so modified that the spreading ability is noticeably improved and the eye lashes appear to increase in size. Moreover, the drying time is also improved.

Thus, the use of DHSA coated pigments in the mascara formulation noticeably improves the curling effect, while reducing the drying time of the applied layer. Pigments coated with Zn-DHSA improve the coating and the volume-increasing effect of the eye lashes.

Deodorant Stick with DHSA

Deodorant sticks are based on alcohol or propylene glycols that are gelled with sodium stearate. Palm DHSA has also been incorporated into deodorant stick formula by combining the potential stick-forming properties of DHSA, and at the same time to determine its key physical properties and the deodorant efficacy (Ismail *et al.*, 2003; 2005a; 2006a). Deodorant bases were prepared in liquid crystalline region, which was obtained from ternary phase behaviour by constructing the phase diagram of DHSA/sodium hydroxide solution/PG at 80°C (*Figure 8*). The area of liquid crystalline region was confirmed under microscope. The DHSA-based deodorant stick was compared with commercial samples as standards. The deodorant stick formulations with DHSA are shown in *Table 6*.

TABLE 5. EYE MASCARA FORMULATION

Ingredient	%
Aqua	54.10
Propylene glycol	3.00
Sodium hydroxide (30% aq.sol)	2.90
Acrylates/octylacrylamide copolymer	5.00
Carnauba	1.00
Candelilla cera	5.00
Cera alba	5.00
Ozokerite	2.00
Stearic acid	5.00
Cetyl alcohol	3.00
Palm oil	3.00
Zinc hydroxystearate coated CI 77499	10.00
Preservants	q.s.

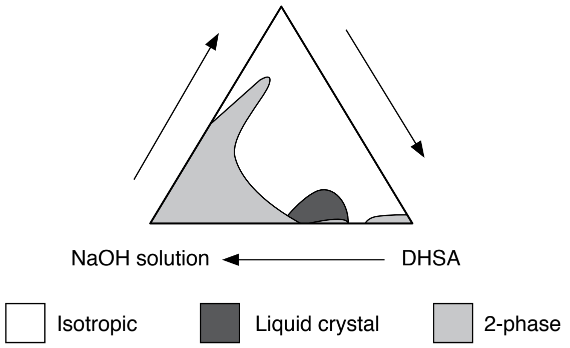


Figure 8. Ternary phase diagram of DHSA/PG/NaOH solution system at 80°C.

The phase changes were observed visually through polariser film and a polariser microscope. The results showed that the anisotropic properties changed from isotropic to lamellar liquid crystals identified as maltese cross patterns and two-phases (*Figure 9*). Deodorant sticks developed based on the maltese cross pattern showed the most stable network.

In general, sticks prepared without alcohol tend to have lower penetrability property (hard stick) than the ones with alcohol type (soft stick) and the colour changes from transparent to translucent (*Figure 10*). The penetrability property, *i.e.* the stick hardness was measured by penetrometer as described in DIN 5179, ASTM Standard Method of Test D 1321-57 and D927-58. A greater distance indicates a softer stick whereas a smaller distance indicates a stronger resistance to penetration and therefore it is harder. The results showed that the formulation without ethanol in F1 had lower penetrability, but with the presence of ethanol as in F2 and F3, higher penetrability (soft stick) was observed as in COM 1 COM 2 and COM 3 products (*Figure 11*).

Figure 12 shows a short disintegration time found in F2 and F3 formulae lay in the range between

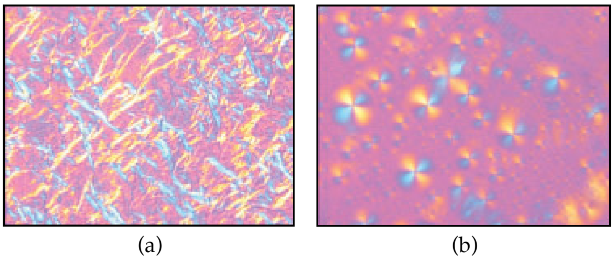


Figure 9. Optical pattern of lamellar liquid crystal at 90:10 of dihydroxystearic acid (DHSA) and NaOH solution at 200X magnification. (a) Oily streaks, (b) maltese crosses.

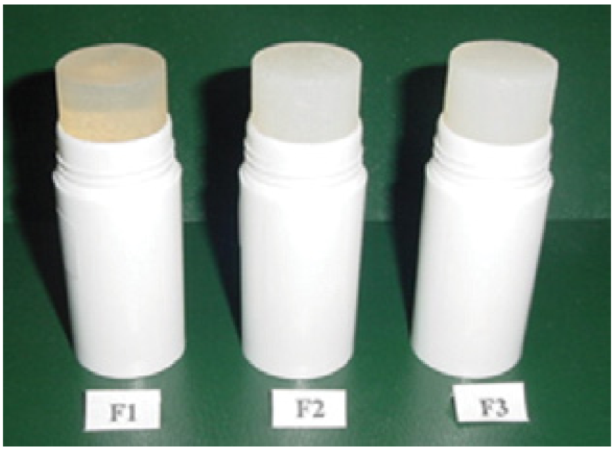


Figure 10. Changes in the appearance of dihydroxystearate–based deodorant sticks dependence on the solvent added, F1 with 100% glycerol; F2 with same amount of ethanol and glycerol; F3 with more ethanol than glycerol.

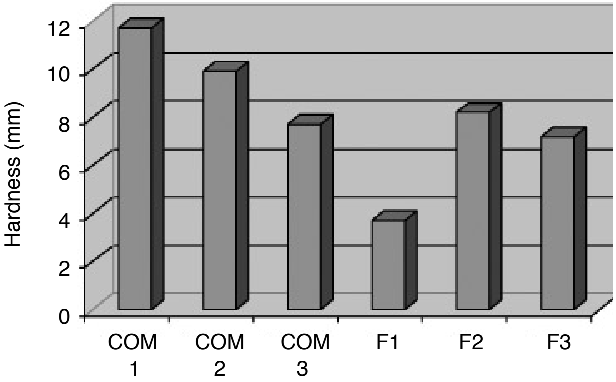


Figure 11. Hardness of deodorant sticks compared with commercial samples.

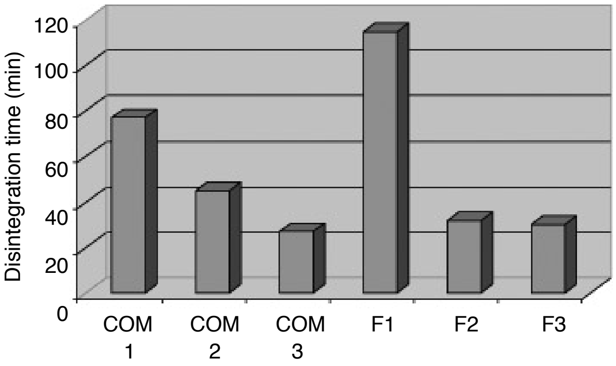


Figure 12. Disintegration time of deodorant sticks compared with commercials samples.

TABLE 6. DEODORANT STICK FORMULATIONS

Formulation	F1 (%)	F2 (%)	F3 (%)
Dihydroxystearic acid (DHSA)	26	26	26
Sodium hydroxide (NaOH) solution	22	22	22
Propylene glycol	3	3	3
Ethanol	-	23	34
Glycerol	46	23	12
Fragrance	3	3	3

products COM 2 and COM 3. Disintegration time is time observed for complete dissolution of the stick placed in enough distilled water to make an 8% w/w solution of the stick mass, measured at 37°C. Based on these results, these formulations could be deployed in preparing medicated sticks. A long disintegration time was found in F1 and this could be suitable for therapeutic sticks preparation.

Table 7 shows that the amount of bound and bulk water were dependent on the percentage of the solvent used in the system. With equal amount of ethanol and glycerol used in F2, the stick was found easy to apply and its hardness lay between products COM 2 and 3. Moreover, the bulk and bound water revealed that formation of three-dimensional gel-liked structure occurred in this system. Product F2 had more bound than bulk water and comparable to COM 1. A short disintegration time was found in F2, and thus it is suitable for medicated stick formula.

DHSA AS A FEEDSTOCK FOR VALUE-ADDED CHEMICALS

The DHSA has three functional groups, *i.e.*, one carboxyl or ester group and two hydroxyl groups located at C9 and C10 on the aliphatic chain. These functionalities may be utilised as follows: (i) at the carboxyl position, through a wide range of esterification, (ii) the hydroxyl group can be acetylated or alkoxylated, (iii) the hydroxyl can be removed by dehydration to increase the unsaturation of the compound or to form polymer, and (iv) the hydroxyl position is so reactive, the molecule can be split at that point by high temperature, pyrolysis and by caustic fusion to form useful product of shorter chain such as sebacic acid, aldehyde or undecenoic acid.

Octyl Dihydroxystearate

Octyl dihydroxystearate (ODHS) is a derivative of DHSA (*Figure 13*). It is produced through enzymatic esterification of palm-based DHSA with n-octanol (Awang and Ahmad, 2000; 2003; Awang *et al*., 2000; 2003; 2004a; 2004b; 2005a; 2006b; 2007a). ODHS is a white, colourless and tasteless compound, made of lustrous crystals. Thus, ODHS is a soft powder with an exceptional skin feel. Indeed, when it is spread over the skin surface, a silky touch is perceived. It has a melting point of 69.9°C.

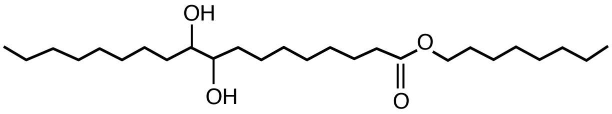


Figure 13. Structure of octyl 9,10 dihydroxyoctadecanoate (octyl DHSA).

Alkanolamides of DHSA

Alkanolamides are non-ionic surfactant in which the hydrophilic (amine) and hydrophobic (fatty acid) moieties are linked via an amide bond. The synthetic reaction scheme between ethanolamine/propanolamine is shown in *Figure 14*. The conversion was as high as 95% for the

TABLE 7. THERMOGRAVIMETRIC ANALYSIS (TGA) – BULK WATER, INTERLAMELLARLY BOUND WATER AND WATER LOSS OF VARIOUS DEODORANT STICKS

Samples	Bulk water (%)	Interlamellarly bound water (%)	Water loss (%)
COM 1	35.6	56.8	7.6
COM 2	37.8	60.5	1.7
COM 3	63.2	34.9	1.9
F1	67.4	26.9	5.7
F2	41.0	53.3	5.7
F3	50.9	43.0	6.1

reaction between DHSA and propanolamine and, 98% for DHSA and ethanolamine after 2 hr reaction time (Awang *et al.*, 2006a). The results suggested that a reaction time of half an hour sufficed for conversion, since product yields of 77% and 87% of DHSA-propanolamide and DHSA-ethanolamide, respectively, were already obtained. However, the product may consist of amine soap, alkanolamide, aminoester and ester amide. DHSA-ethanolamide and DHSA-propanolamide were detected at retention times of 15.65 min and 16.61 min, respectively by gas chromatography analysis. *Table 8* shows the properties of DHSA-alkanolamides.

Surface tension of DHSA-ethanolamide and DHSA-propanolamide are 35 mNm^{-1} and 39 mNm^{-1}, respectively, which is lower than surface tension of deionised water (70.19 mNm^{-1}). The DHSA-ethanolamide had better foaming power and stability than DHSA-propanolamide. The DHSA-alkanolamides could be used as foam improver when added to the solution containing sodium dodecyl sulphate (1%, w/v) (Awang *et al.*, 2006a).

Estolides of DHSA

Estolide is a polyfunctional oligomer that contains ester linkages on the alkyl backbone of the molecule, which is formed by the esterification reaction between fatty acids. These ester linkages are more resistant to hydrolysis than those of triglycerides. The unique structure of the estolides makes it to have superior physical properties if compared to the mineral and vegetable oil in certain applications. Estolides can be potentially used in a variety of applications, such as surfactants, ingredient and additive in cosmetic and inks formulation. An attempt was made to synthesise dihydroxystearic acid-estolide (DHSA-estolide) from palm-based DHSA through a condensation reaction (*Figure 15*). The hydroxyl and carboxyl groups in DHSA reacted inter-molecularly to form DHSA-estolide. The condensation of DHSA at various reaction periods yielded product mixtures with high saponification values but low acid values indicating fatty acid had been successfully converted into the ester. As the reaction proceeded, the powdery DHSA changed to a sticky and hardly pourable paste. This was due to homo-oligomerisation of DHSA which produced DHSA-estolide with higher molecular weight than that of the starting material. The increased average molecular weights [calculated based on the neutralisation equivalent (NE) and end-group analysis] of the product obtained, indicated the repeating unit or molecular weight of the DHSA-estolide produced, increased with increasing reaction period. The low peroxide values of DHSA-estolides show that they are oxidatively stable (Awang *et al.*, 2005b; 2007b).

Analyses of gel permeation chromatography and high performance liquid chromatography showed that the product obtained were actually a mixture of DHSA and DHSA-estolides of different repeating unit. Fourier transform infra-red (FTIR) and nuclear magnetic resonance (NMR) analyses

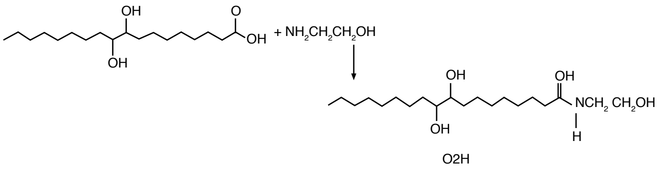


Figure 14. Reaction scheme of dihydroxystearic acid (DHSA) and ethanolamide.

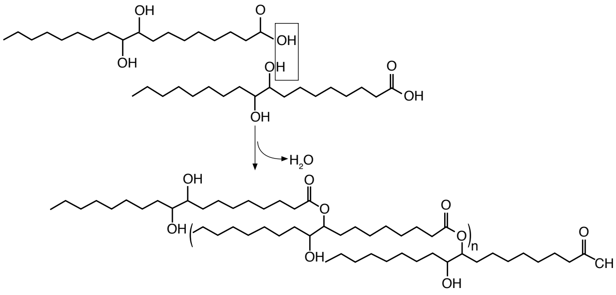


Figure 15. The condensation of dihydroxystearic acid (DHSA) to produce DHSA estolide.

TABLE 8. PROPERTIES OF DIHYDROXYSTEARIC ACID (DHSA) ALKANOLAMIDES

	Alkanolamides of DHSA	
	Monoethanolamide	**Monopropanolamide**
Colour	Yellowish	Yellowish
Acid value (mg KOH g^{-1})	1.05	2.18
OHV (mg KOH g^{-1})	281.25	267.71
Melting point (°C)	83-85	84-86
Ecotoxicity	22.63	22.63
Solubility	Soluble in water	Soluble in water
Irritancy	Non-irritant	Non-irritant

confirmed the formation of estolide. The esters transmittance peaks (1733 cm^{-1}-1742 cm^{-1}) with an acid shoulder (1713 cm^{-1}-1716 cm^{-1}) were observed in FTIR spectrum. The ester methane signal at 4.84 ppm was an indication of an estolide linkage in the H-NMR while the ^{13}C-NMR showed two carboxyl signals at 178.78 ppm for acid and 172.08 ppm for estolide.

These DHSA-estolides are found applicable as anti-rust additive in cutting fluid. The DHSA-monoestolide and DHSA-diestolide with the acid value of 60-90 mg KOH g^{-1} are found compatible in shampoo formulation and improve the performances of the shampoo. DHSA-tri-estolides and DHSA-pentaestolides with the acid value of 20-40 mg KOH g^{-1} are found fully functional as emulsifier and thickener in water-in-oil emulsion for cosmetic formulation (Awang *et al*., 2007c).

Monoglycerides of DHSA

Monoglycerides of DHSA was synthesised by reacting DHSA with glycerol in the presence of catalysts. Various factors, such as reaction temperature, reaction time, catalyst concentration and types of catalysts that may affect the esterification reaction were studied (Awang *et al*., 2009). A mixture of monoglycerides (MG) and diglycerides (DG) of DHSA was obtained when the reaction was carried out at 150°C for 4 hr in the presence of p-toluene sulphuric acid (p-TSA) as a catalyst. The composition of MGDHSA and DGDHSA were increased with increasing reaction temperature from 100°C to 180°C (*Table 9*). Different result was observed for the effect of catalyst concentration (*Table 10*). A higher acid concentration caused a higher degree of the unwanted polymerisation and a decreased formation of the MGDHSA. The presence of excess catalyst may promote polymerisation reaction of glycerol rather than esterification of glycerol and DHSA.

The reaction product containing ~45% MGDHSA was found to be non-irritant to the skin, with HIE (Human Irritancy Equivalent) score below 0.90. The MGDHSA degraded by more than 60% in 20 days, which is considered readily biodegradable. This compound was non-toxic to the aquatic environment for which the toxicity value was more than 100 mg $litre^{-1}$. The MGDHSA was dissolved in various types of cosmetic oils by heating. Emulsions using MGDHSA as an emulsifier showed higher stability in the system with higher water content compared to the emulsion system containing MGHSA and GMS as an emulsifier.

Polyethylene Glycol Esters of DHSA

Polyethylene glycol (PEG) ester is a mono- or diesters of fatty acid or oil reacted with a PEG. It has been widely used as emulsifiers, pearlisers, stabilisers, solubilisers or viscosity-controlling agent in household and cosmetic products such as lotion, cream, shampoo, *etc.* Owing to its versatility in different field of application, numerous efforts have been contributed towards improving the existing PEG types with improved properties. The PEG ester of DHSA was prepared by esterifying PEG with DHSA or DHSA estolides at a temperature of 120°C to 200°C in the absence of catalyst (Awang *et al*., 2008; 2012). Mole ratios of starting materials play important role in determining the reaction product mixture, where to produce higher percentage of monoester, excess PEG is required, whereas for producing higher diester in the product mixture, excess DHSA/acid is required. The hydroxyl groups presented in the alkyl chain are not affected or modified by the end of the esterification process, where transmittance peak of hydroxyl group can still be observed at ~3300 cm^{-1} wavenumber in FTIR spectrum. *Table 11* shows the use of PEG-DHSA ester and PEG-DHSA estolide ester as wetting agent, while *Table 12* indicates the use of PEG ester as a soil remover agent.

DHSA Ethoxylates

An exploratory experiment has also been carried out to ethoxylate DHSA as indicated in the following reaction scheme (*Figure 16*). *In vitro* dermal irritection assay test indicated that DHSA

TABLE 9. EFFECT OF REACTION TEMPERATURE ON COMPOSITION OF THE PRODUCT*

Temperature (°C)	Acid value (mg KOH g^{-1})	%	
		MGDHSA	DGDHSA
100	137.37	11.84	1.04
120	109.40	18.19	1.64
150	67.97	43.55	8.90
180	9.71	72.91	12.39

Note: *Reactions were carried out for 4 hr in the presence of 0.5% (w/w) p-TSA as catalyst.
The ratio of dihydroxystearic acid (DHSA) to glycerol is 1:6.
MG - monoglyceride. DG – diglyceride.

TABLE 10. EFFECT OF CATALYST CONCENTRATION ON COMPOSITION OF THE PRODUCT*

Catalyst (%)	Acid value (mg KOH g^{-1})	%	
		MGDHSA	DGDHSA
0.0	99.94	36.90	8.99
0.2	69.84	43.72	10.25
0.4	64.19	43.50	10.96
0.6	58.67	41.90	10.58
0.8	55.78	40.61	12.35
1.0	18.01	21.25	0.00
2.0	8.09	0.00	0.00

Note: *Reactions were carried out at 150°C for 4 hr in the presence of various concentration of p-TSA as catalyst. The ratio of dihydroxystearic acid (DHSA) to glycerol is 1:6. MG - monoglyceride. DG – diglyceride.

TABLE 11. USE OF PEG-DHSA ESTER AND PEG-DHSA ESTOLIDE ESTER AS A WETTING AGENT

PEG esters	Wetting time (s)
DHSA-PEG200	27
DHSA-PEG300	17
Diestolide-PEG200	48
Triestolide-PEG200	88

Note: PEG - polyethylene glycol. DHSA - dihydroxystearic acid.

TABLE 12. USE OF PEG ESTER AS A SOIL REMOVER

Sample	Water hardness (ppm)		
	50	150	350
DHSA-PEG200	21.63%	18.06%	16.92%
DHSA-PEG300	20.75%	19.29%	18.41%
Diestolide-PEG200	23.69%	20.77%	21.28%
Triestolide-PEG200	10.53%	6.60%	5.88%

Note: PEG - polyethylene glycol.

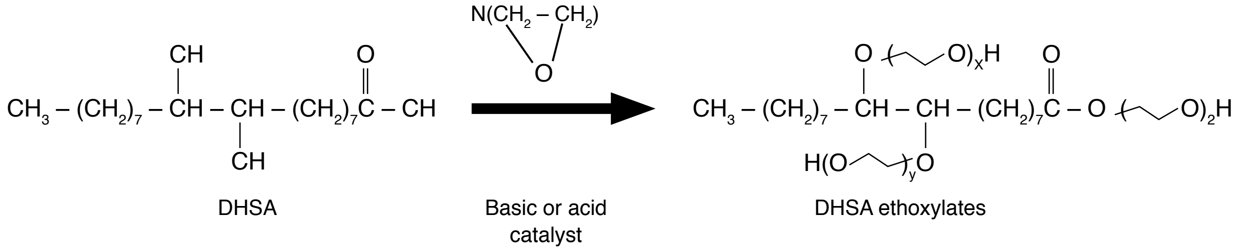


Figure 16. Reaction scheme of dihydroxystearic acid (DHSA) and ehtylene oxide.

ethoxylates with various moles of ethylene oxide (5EO, 10EO, 15EO and 20EO) are non-irritant. It was also found that DHSA ethoxylates have the potential to be used in transparent soap, detergent and in rigid polyurethane formulations (unpublished data).

APPLICATION OF DHSA DERIVATIVES

ODHS in Make-up Products

In facial powder make-up products, fats have always been used at a low concentration from 2% to 10%. The reason for such limited use is easily understood: a very thin fatty layer is required, just enough to 'wet' the surface of the powder granules, in order to provide easy flow and lubrication among granules. Minimal use of fats also helps to reduce dustiness during the application phase, as well as establishing a good adhesion between superficial skin lipids and the pigmented powder. Moreover, such layer avoids skin dryness due to water intake from the skin and reduces the absorption of sweat and sebum into powders. The distribution process of fats (called binders) onto powder particles is made easy by the abundant use of talc in the formulae, an ingredient that provides high affinity for lipids.

As the chemical reactivity in such a system is high (very extended surface, presence of pro-oxidant metallic ions, high amount of oxygen adsorbed onto the pigments and fillers surface, milling procedures carried out in turbulent air), hydrocarbons and saturated lipids are the preferred oil category. The low percentage of use does not allow them to be 'squeezed out' from the granules in the compact cake, so avoiding the formation of hardened plaques.

The application of octyl dihydroxystearate (ODHA) in compact eye shadow with high content of mica and pearls is reported here (*Table 13*).

ODHS is an advantageous ingredient for the formulations of many make-up products (Chua *et al*., 2006; 2007) where it acted as a thickening agent in most of the formulations studied. The uniformity of the traces were improved together with a more rich, silky and non-oily feel on the skin. Besides, ODHS also increases product adhesion and lasting effect on the skin.

Some other ternary phase diagram studies have also been carried out to look into the characteristics and morphology of various combinations of DHSA and ODHS with other lipids such as RBD palm kernel olein (RBDPKOo), medium chain triglycerides (MCT) as the basis for cosmetic and personal care formulations (Ismail *et al*., 2005b; 2008; Kassim *et al*., 2004; 2007). Results have shown that all ratios of DHSA/ODHS were completely in two-phase region with various concentrations of RBDPKOo/MCT and needles and spherulite textures were found in this system.

TABLE 13. COMPACT EYE SHADOW

Ingredient	%
Mica	To 100
Talc	4.00
Mica/methicone	7.00
CI 77492	4.50
CI 77491	2.85
Preservatives	q.s.
Pearls (mica + titanium dioxide)	17.80
Octyl dihydroxistearate	9.00

CONCLUSION

DHSA and its new derivatives, made from renewable sources, can find sensory related and technical applications in cosmetics, especially those products that require the use of pigments. In all these cases, better performances are observed that are related to oil phase thickening, skin adhesion, pay off, and skin feel properties. The presence of polar groups allows DHSA to be easily adhered to solids. Stable deposition can be improved by converting it into metallic soaps through divalent and trivalent metal salts. DHSA derived metallic soap shows remarkably new behaviours and the best properties are demonstrated by Zn and calcium-based soaps.

DHSA modifies the adsorbing and absorbing power of pigment surfaces. As a coating agent, the dispersion of pigments is made easier, as it improves their wettability. Indeed, this provides better colour performances and shade reproducibility.

DHSA has interesting application and sensorial characteristics: in lipsticks it improves brightness and enhances long-lasting characteristics, and when used in the wax phase, it improves pay-off and distribution properties as well as increasing the stick strength. Zinc DHSA, used as coating, reduces the motorboat effect in lipsticks, as it provides a better co-ordination of the lipid phase. In lip gloss, zinc DHSA coating improves noticeably the trace distribution and homogeneity of the product after application.

DHSA coated pigments used in water-in-oil (W/O) emulsions such as mascara, significantly improve the curling power and reduce the drying time; if the coating is made of zinc DHSA, better spreadability over lashes and a significant volumising effect is obtained. In oil-in-water (O/W) emulsions such as foundations, DHSA pigment coating provides emollient effect, better softness, easy application and good covering power, whereas zinc DHSA coating provides dry feel and more transparency characteristic.

In compact powders, DHSA coated pigments increases powder hydrophobicity, providing velvety skin-feel and increasing the adhesion of the product onto the skin. Zinc DHSA coating improves product application with lighter adhesion characteristics.

As an additive in a transparent soap formulation, DHSA has been found to enhance the transparency of the soap. The DHSA also has the potential application as thickener and gelling agents and thus can be used to prepare deodorant sticks.

Besides, DHSA is also a potential feedstock for various value-added derivatives through substitution reactions onto one, two or all three of the reactive sites. Some alkyl esters from DHSA have been studied, which show exceptional skin-feel and powder binding capability. The DHSA derived metallic soaps have been prepared that show pigment coating capability and a set of different properties are observed when compared to the usual metallic stearates. Many more derivatives of DHSA, such as DHSA esters, estolides, alkanolamide, monoglycerides have been derived to exploit all the possible applications of DHSA as feedstock. In conclusion, this review has shown the value addition potential of palm DHSA produced from oleic acid, a low value by-product of the Malaysian oleochemical industry.

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