IMIDAZOLINE AMPHOTERIC SURFACTANTS FROM PALM AND PALM KERNEL FATTY ACIDS

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Various imidazoline–type amphoteric surfactants were synthesized based on palm oil and palm oil products. The surface active parameters of the surfactants such as surface tension, anti-static, electrical conductivity, dispersing power, wetting power, anti-rust and anti-microbial action were determined. The advantages of palm-based amphoteric surfactants in terms of anti-static, dispersing and wetting power and rust-prevention properties were described.

INTRODUCTION

A number of reports on the imidazoline amphoteric surfactants have been published (Christiansen, 1982). Amphoterics are being produced industrially as bases for shampoos and cosmetics because they can be combined with any other type of surfactant over a wide range of pH, and they are less irritating to the human skin and eyes than some other surfactants.

The commercial products are mainly derived from coconut fatty acids, and more rarely from tallow fatty acids. Similar products from palm and palm kernel fatty acids have not been reported. The imidazoline amphoteric surfactants can be synthesized by the procedure shown in *Figure 1*. The general commercial products do not consist only of a single compound (III), since they are made from mixtures of fatty acids, and they also contain various intermediates and side reaction products.

In order to expand the downstream application of palm-based oleochemicals, the reaction to produce imidazolines from palm oil and palm kernel oil fatty acids was studied. The imidazoline derivatives from C12-, C16-, and

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C18- fatty acids were also made, and a sample from tallow fatty acid was prepared for purposes of comparison.

The products were evaluated for the various surface active properties. As references, a standard surfactant, sodium dodecyl sulphate (SDS) and a commercial amphoteric T (from Japan) were used. The surface active properties of the amphoterics were evaluated in PORIM and the National Chemical Laboratory for Industry (NCLI) in Japan.

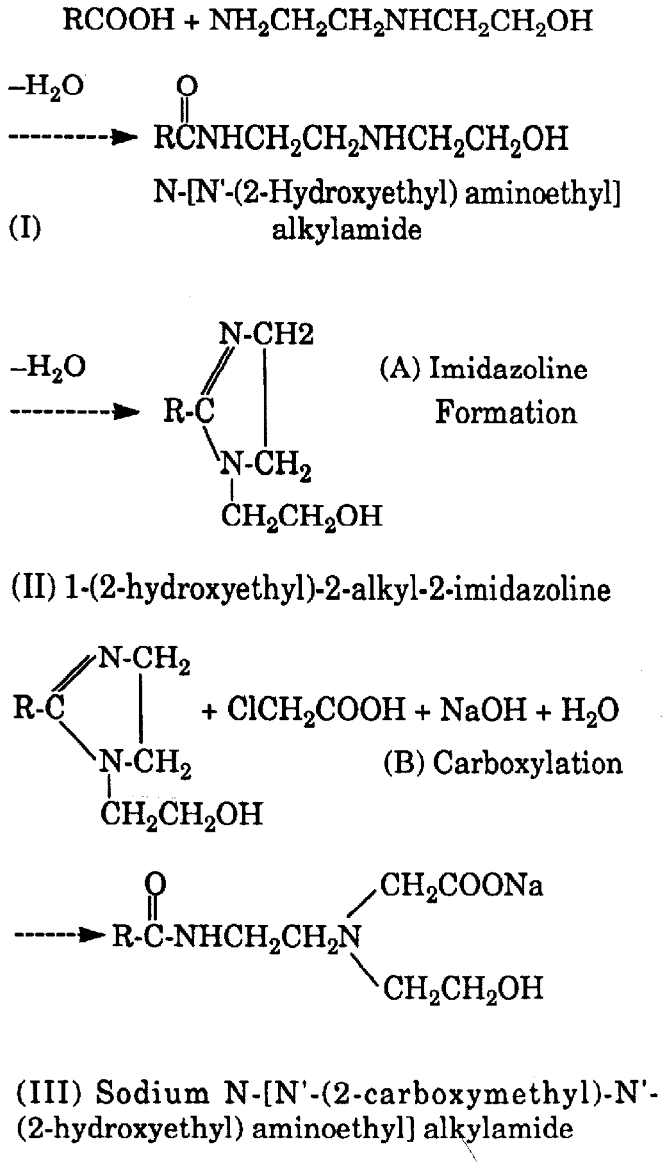

Figure 1. Synthesis of the Alkyl Imidazoline Amphoteric Surfactants

MATERIALS AND METHODS

Materials

Palm, palm kernel and tallow fatty acids were supplied by Southern Acid (M) Sdn. Bhd. Lauric, palmitic and stearic acids were obtained from Acidchem Sdn. Bhd. The acid values of these materials and the purities of the individual acids determined by GC are shown in *Table 1*.

N-(2-Aminoethyl) ethanolamine (AEEA) (99%) was obtained from Nakarai Chemicals Co. of Japan, whilst chloroacetic acid (99%), was acquired from Sigma Chemical Co. USA.

Alkylimidazoline formation, (A) (*Figure 1*).

Each fatty acid or fatty acid mixture (0.2 mole) was treated with AEEA (0.24 mole) and the reaction mixture was heated gradually to 200°C. Heating at 200°C was continued with the bubbling of nitrogen for 4.5 hours under reduced pressure of 50 mmHg and 1- (2-hydroxyethyl) -2-alkyl-2-imidazoline was obtained.

During the reaction, samples of the mixture were withdrawn at 1.5 hour intervals and the infra-red spectrum, and the amine and free fatty acid contents of the samples were determined. The amine contents were determined according to the AOCS official method, Tf 3a-64.

TABLE 1. ACID VALUES AND PURITIES OF FATTY ACIDS

	Acid Value	Purity (%)
Palm fatty acids	192.2	–
Palm kernel fatty acids	235.5	–
Tallow fatty acids	195.9	–
Lauric acid	283.9	98.2
Palmitic acid	225.4	94.0
Stearic acid	197.7	98.4

Carboxylation, (B) (*Figure 1*)

Chloroacetic acid (0.28 mole) was dissolved in 100 ml of water. This was added to the 1-(2-hydroxyethyl) -2-alkyl-2-imidazoline, *i.e.* the reaction product from the previous step, and the solution was heated to 80°C while stirring. A clear light yellow solution was obtained; when the pH of the solution fell to 9, 0.28 mole of sodium hydroxide in 50% aqueous solution was added dropwise while stirring, still at 80°C. The pH of the reaction mixture was maintained at pH 8-10 during the addition. Stirring was continued for one hour after completing the addition of the base and sodium N-[N'-(2-carboxymethyl)-N'-(2-hydroxyethyl) aminomethyl] alkylamide was obtained.

Determination of Surface Active Properties

The surface tensions of surfactant solutions which were adjusted to pH 5, 7 and 10 were determined at 25°C with a Shimadzu ST-1 surface tension meter. The foaming powers of 0.1% solutions were determined by pouring each of them into a 500 ml measuring cylinder and whipping with a perforated plunger, giving 30 constant vigorous strokes by hand. The volume of the foam produced was read immediately and after five minutes.

Electrical conductivity was measured with a TOA Digital Conduct Meter model CM-15A on 1% solutions and 0.1% solutions of a few selected samples.

Anti-static properties were tested on four types of cloth, namely: nylon, cashimilon, tetron and pylen with a Digital super Megaohm Meter model DSM-515A and Electrode for Flat Solid Sample model SME-10-5. Before measurement the cloths, treated with surfactant solutions, were kept in a dry box (< 1% RH) for three hours or a wet box (93% RH) overnight to obtain the respective humidities. Measurements were carried out under the two different RH's

To measure the dispersing power, carbon black and titanium dioxide were used. They were added separately to 1% surfactant solutions, and the mixtures were shaken and allowed to stand. Evaluations were carried out by looking at the height and cloudiness of each solution and noting the scores.

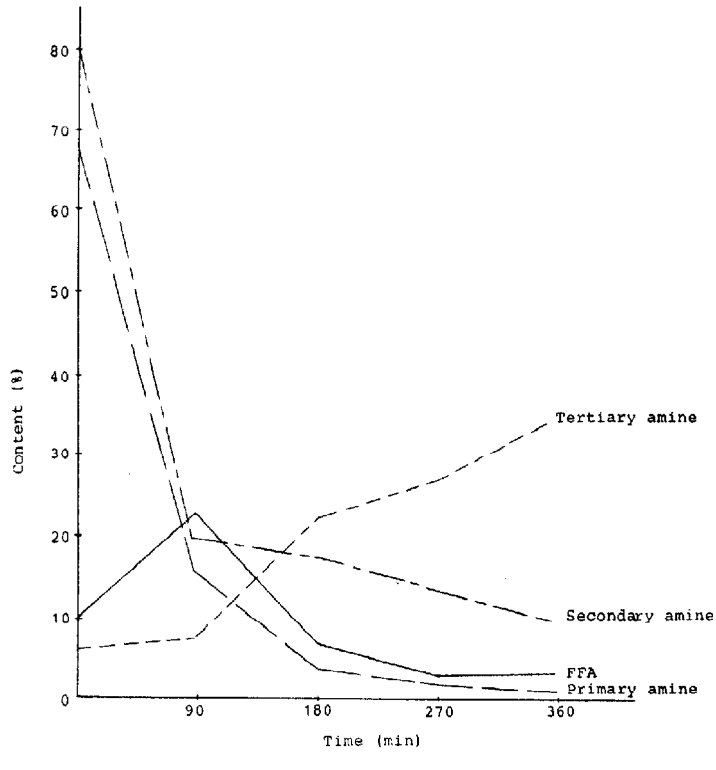

Figure 2. Changes in content of primary, secondary and tertiary amines and free fatty acid in reaction mixture based on palm kernel fatty acids.

Felt cloth was used for the measurement of wetting power, small pieces being placed on the surface of a surfactant solution. The time taken for the piece of cloth to sink into the solution was measured.

Rust preventive power was assessed by observing the changes on an iron surface in a surfactant solution of various concentrations, and the anti-microbial properties were gauged by observing the growth of microbes.

RESULTS AND DISCUSSION

Imidazoline Formation

Changes in the contents of primary amine (AEEA); secondary amine (N-[N'-(2-hydroxyethyl) aminoethyl] alkyl-amide) and tertiary amine (sodium N-[N'-(2-carboxymethyl)-N'-(2-hydroxymethyl) amino-ethyl] alkylamide), and the content of free fatty acids (FFA) in the reaction mixture during the reaction are shown in *Figures 2, 3* and *4*. The monoamide derivative (N-[N'-(2-hydroxyethyl) aminoethyl] alkylamide) was formed initially by condensation, with the elimination of water, and it then cyclized to imidazoline derivatives (1-(2-hydroxyethyl)-2-alkyl-2-imidazoline). The contents of secondary amine (N-[N'-(2-hydroxyethyl) aminoethyl] alkylamide) decreased, and that of tertiary amine (1-(2-hydroxyethyl)-2-alkyl-2-imidazoline) increased with reaction time. FFA and AEEA had practically disappeared, and the reaction (A) was considered to be almost complete after 4.5 hours.

No significant differences were noted between the behaviour of palm, palm kernel and tallow fatty acids during the reaction producing imidazolines. The general forms of the curves from the three different sources of fatty acid are very similar and such small variations as can be seen are possibly due to the fact that reaction conditions could not be kept exactly uniform from one experiment to another.

The products obtained were pale yellow viscous liquids with a slight amine odour; they showed a peak of C=N at 1610 cm^{-1} in their IR spectra.

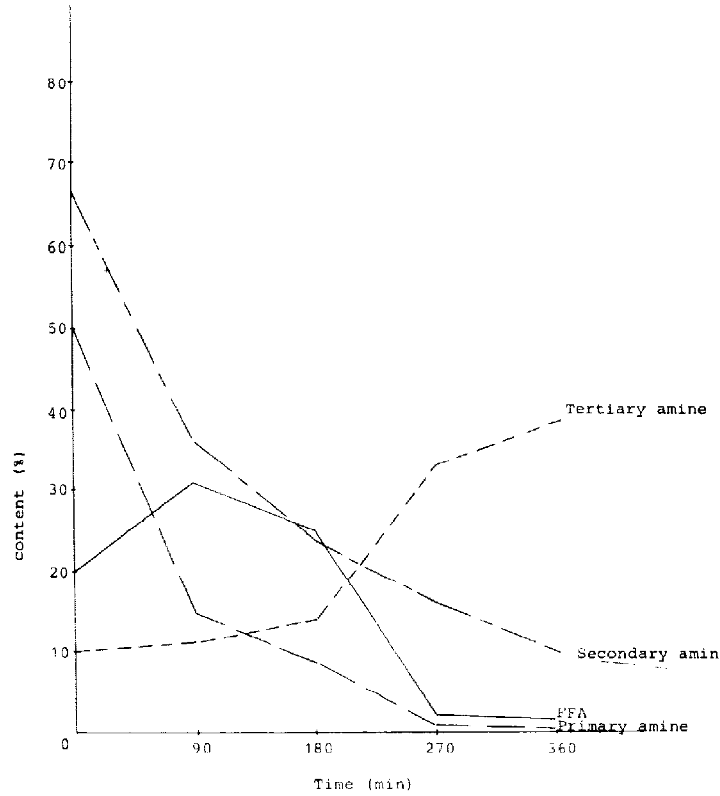

Figure 3. Changes in content of primary, secondary and tertiary amine and free fatty acid in reaction mixture based on palm oil fatty acids.

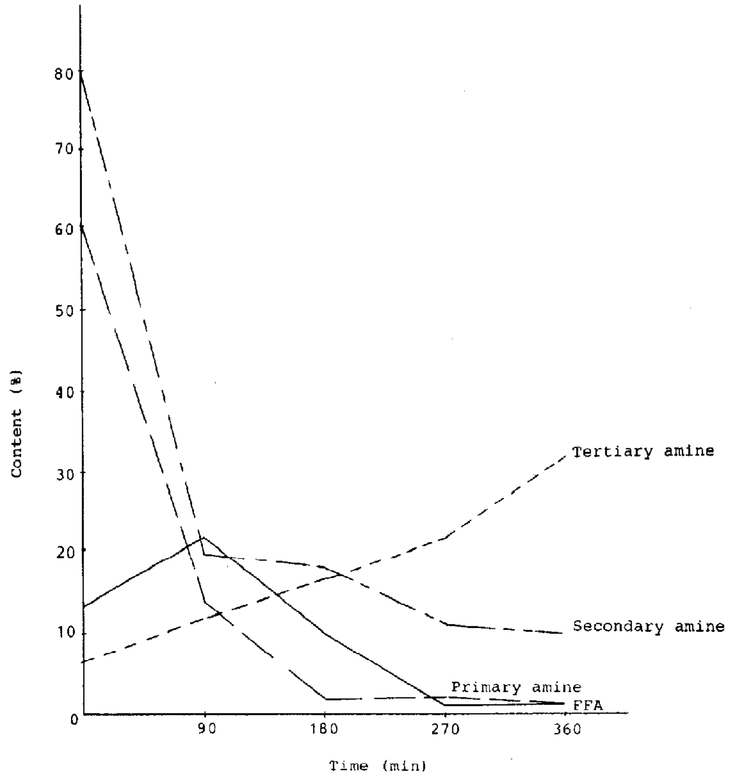

Figure 4. Changes in content of primary, secondary and tertiary amines and free fatty acid in reaction mixture based on tallow fatty acids.

TABLE 2. SURFACE TENSIONS AND CRITICAL MICELLE CONCENTRATIONS (cmc) OF SAMPLES OF AMPHOTERICS AT VARIOUS pH VALUES

Starting material	**pH5**		**pH7**		**pH10**	
	cmc × 10^3 mol/l	**Surface tension (dyne/cm^2)**	**cmc × 10^3 mol/l**	**Surface tension (dyne/cm^2)**	**cmc × 10^3 mol/l**	**Surface tension (dyne/cm^2)**
Lauric acid	0.27	28	0.27	31	0.27	32
Palmitic acid	0.24	30	0.24	31	0.24	32
Stearic acid	0.28	31	0.28	32	0.28	33
Palm kernel fatty acids	0.17	27	0.17	27	0.17	30
Palm oil fatty acids	0.21	30	0.14	29	0.12	31
Tallow fatty acids	0.25	32	0.25	31	0.25	32

TABLE 3. ANTI-STATIC VALUES OF SAMPLES AT 93% RH AND <1% RH

	Nylon		Cashimilon		Tetron		Pylen	
Sample	**93%RH**	**<1%RH**	**93%RH**	**<1%RH**	**93%RH**	**<1%RH**	**93%RH**	**<1%**
Amphoteric from :								
Lauric acid	4.3×10^8	3.0×10^{10}	1.2×10^8	6.9×10^7	1.2×10^8	4.4×10^7	1.3×10^8	3.9×10^7
Palmitic acid	2.4×10^7	1.7×10^9	1.1×10^7	9.9×10^8	2.1×10^6	1.0×10^9	2.8×10^7	3.9×10^8
Palm oil fatty acids	9.0×10^7	1.7×10^9	1.5×10^8	3.1×10^8	1.8×10^8	2.1×10^8	2.1×10^8	1.9×10^8
Amphoteric T	2.3×10^7	7.4×10^8	1.7×10^7	3.8×10^8	1.9×10^6	2.8×10^8	3.3×10^7	8.1×10^9
SDS	3.3×10^{10}	1.0×10^{11}	7.1×10^8	3.1×10^8	$>2.3 \times 10^{12}$	1.6×10^{12}	1.3×10^{10}	1.0×10^9

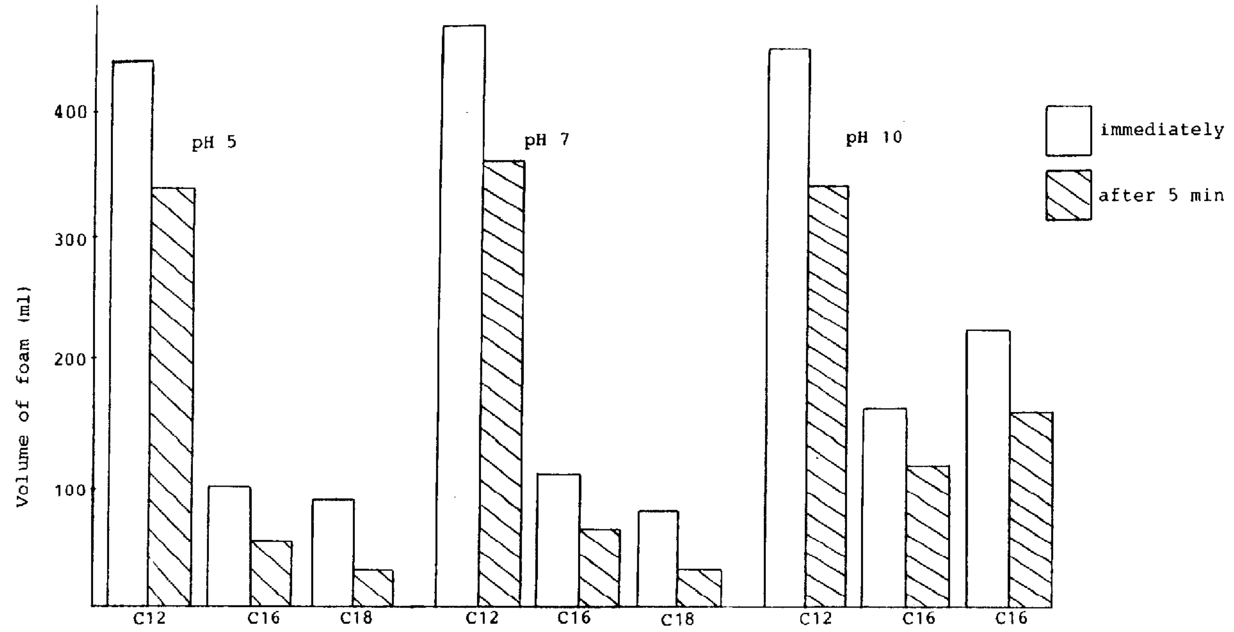

Figure 5. Foaming power of samples at various pH values. C12, C16, C18 refer to samples made from lauric, palmitic and stearic acids respectively.

Carboxylation

Most amphoteric imidazoline surfactants are produced commercially by carboxylation with chloro-alkylcarboxylate in aqueous alkaline media under ring-opening conditions as shown (B) in *Figure 1*. In the present study, the alkyl imidazoline was carboxylated according to the method of Tomidokoro (1978), in which the pH of the reaction mixture is kept between pH 8 and 10 during reaction until the final amphoteric surfactants are obtained.

In this step, as in step A, there were no significant differences between the performances of palm, palm kernel and tallow fatty acids as the starting materials.

Surface Active Properties

Aqueous solutions of each product were prepared and the pH was adjusted to 5, 7 and 10 with 10% aqueous solutions of hydrochloric acid or sodium hydroxide. The critical micelle concentrations (cmc), in moles per litre, and the surface tensions (dyne/cm^2) of each solution are shown in *Table 2*. Their foaming powers are shown in *Figure 5*.

The electrical conductivity values of the 1% surfactant solutions were high. This was because samples contained inorganic substances notably sodium chloride. A similar result was shown by the commercial sample T.

Antistatic properties are greatly influenced by temperature and humidity, so that control of these parameters is very important during measurement. The antistatic properties of the palm-based amphoterics and the commercial sample T on the four types of cloths were found to be better (*i.e.* showed lower values) than the standard surfactant SDS. The antistatic values at 93% RH are normally lower than at <1% RH. The results are shown in *Table 3*.

Palm-based amphoterics had good dispersing power with carbon black and titanium dioxide but the dispersing power of SDS with titanium dioxide was better. The C16 sample had the best dispersing power.

The C12 amphoteric showed a better wetting power than sample T, followed in order by samples prepared from palm kernel oil and palm oil fatty acids.

Amphoterics usually have strong anti-microbial action, but in this study neither the palm-

TABLE 4. ELECTRICAL CONDUCTIVITY, DISPERSING POWER AND WETTING, ANTI-RUST AND ANTI-MICROBIAL PROPERTIES OF SAMPLES

Sample	**Electrical conductivity (μS/cm)**	**Dispersing power (CB,TiO$_2$)**		**Wetting power (sec)**	**Anti-rust (ppm)**	**Anti-microbial (ppm)**
Amphoteric from :						
Lauric acid	3080	4.0	4.5	6.9	500	–
Palmitic acid	2250	4.5	4.5	>200	>1000	>1000
Palm kernel oil fatty acids	2740	4.0	4.5	16.9	500	>1000
Palm oil fatty acids	2190	–	–	35	50	>1000
Tallow fatty acids	2510	–	–	94.2	100	–
Amphoteric T	2800	4.0	4.5	23.1	500	>500
SDS	1240	4.5	3.5	117.2	>500	200

based amphoterics nor the commercial sample T showed any anti-microbial properties. SDS, however, displayed a good anti-microbial action.

The rust-preventive power of amphoterics is not very clear since they contain salt. However the palm-based amphoterics showed good rust-preventive power especially the sample from palm oil fatty acids. SDS and sample T did not show any rust-preventive properties.

CONCLUSIONS

1. The reaction conditions for the production of palm-based imidazoline amphoteric surfactants were established.
2. No significant differences were observed in the synthesis of the surfactants from palm and palm kernel fatty acids as starting materials by comparison with the synthesis from tallow fatty acids.
3. The palm-based imidazoline amphoteric surfactants showed superior surface active performance over a wide range of pH as compared to that of the tallow-based product.
4. The palm-based imidazoline amphoteric surfactants showed good antistatic, dispersing, wetting and rust-prevention properties but no anti-microbial effect.

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