Quality Parameters for Sodium Cocoyl Isethionate

By DR. ROBERT B. LOGIN
Technical Director
Jordan Chemical, Folcroft, PA

Sodium cocoyl isethionate (SCI), originally described by Daimler and Platz (U.S. Patent No. 1,881,172) in 1932, has been of commercial interest for more than 50 years. It exhibits properties such as high melting point and ease of plodding (moldability) that have resulted in commercial applications centering around its use in syndet and combination toilet bars.

Not only is SCI an effective lime soap dispersant, it is very mild and well tolerated by individuals who are adversely affected by high pH soap bars. Furthermore, it cleans without excessively drying the skin. Its mildness, rich creamy foam and compatibility with perfumes and emollients are readily apparent to those who formulate with it. The success of Lever Brothers' Dove and Caress bars attest to its commercial significance.

New formulations employing SCI either in combination or syndet bars appear regularly; for example, its ability to clean safely at lower pH has made it a prime ingredient in Johnson and Johnson's new baby bar.

Two Methods of Preparation

SCI is commercially prepared by two routes. In one case, the starting coconut fatty acids are converted to the corresponding acid chlorides and subsequently condensed with anhydrous sodium isethionate. Hydrochloric acid is formed as a byproduct and is removed by distillation. Residual hydrochloric acid is neutralized, hence, SCI prepared by this route is characterized by a sodium chloride residue and neutral pH.

By the direct route, coconut fatty acids are condensed directly with sodium isethionate at high temperatures (220-250°C) to afford the ester in molten form. In this procedure, the easily oxidized molten product must be cooled and converted to the finished powder without darkening. It is extremely difficult to reach the activity associated with the acid chloride route; however, the direct route does not produce sodium chloride. It does produce more free fatty acids, hence an SCI with a lower pH specification. Also, because of the vigorous conditions required, some loss of low molecular weight volatile fatty acids can occur.

TABLE 1
Sodium Isethionate

Quality Characteristic	Tolerance
Appearance	Clear, clean liq.
Color, APHA	25 max.
Sodium Sulfite	500 ppm max.
Iron	10 ppm max.
pH as is	9.0-10.0
Actives	56.0% min.
Sodium Sulfate	0.25% max.
Sodium Chloride	0.10% max.
Moisture	44.0% max.
Ethylene glycol	0.40% max.
Diethylene glycol	0.10% max.
Oxidants as H_2O_2	25 ppm max.

Whether produced by the acid chloride or direct route, SCI quality begins with the proper choice of raw materials. Sodium isethionate is commercially available as a 57% solution, the concentration at which it will remain stable and not crystalize upon storage (Sexton, U.S. Patent No. 2,810,747). *Table 1* lists those specifications and tolerance associated with a high quality sodium isethionate solution.

Sodium isethionate is produced by the condensation of sodium bisulfite and ethylene oxide. The reaction takes place readily in water; however, high pH will generate ethylene glycols. They will esterify by either SCI manufacturing route to form mono and diesters that are associated with defoaming. In addition, Geitz (U.S. Patent No. 2,894,912) and Lamberti (U.S. Patent No. 4,003,925) claim that glycols can reduce the viscosity of the wet-mixing step "causing the batch to become soupy thereby leading to increased sandy bar production." Therefore, glycols must be kept to a minimum.

Various grades of coconut fatty acids can be considered; however, Geitz points out the advantages of employing a hydrogenated coconut fatty acid as the raw material of choice. More fully hydrogenated or distilled grades are more expensive and are not required ultimately for soap bar use. Hydrogenated coconut fatty acid-based SCI produces harder bars with better foaming properties and is less susceptible to oxidation and odor formation (rancidity). Some unsaturation is, however, desirable for better bar texture and plasticity; therefore, Geitz recommends an Iodine number between 3.5 and 7.5.

Since the acid chloride route does not affect the fatty acid distribution, whatever is used finds its way into SCI in the same relative ratios; the direct condensation reaction is conducted under conditions in which the alkyl distribution can be altered. For example, Holland and McCrimlisk (U.S. Patents No. 3,420,857 and 858) show how some loss of C_8 and C_{10} fatty acids can be tolerated. In fact, free C_8 and C_{10} fatty acids are associated with SCI products that exhibit increased skin irritation, odor and poor soap bar processing. Cahn (U.S. Patent No. 3,394,155) details the effect of unreacted "low ends."

Comparing Vendor, Consumer, CTFA Specifications

At this point, it is enlightening to compare published product specifications. *Table 2* illustrates these and compares them to a typical consumer and CTFA specification.

The average molecular weight for SCI based on the coco-

TABLE 2
Comparison of Sodium Cocoyl Isethionate Specifications

Specifications (1)	A	B	C	D	Consumer	CTFA
	Vendors					
Mol. Weight	338	338	338	345 + 3	338	341
Assay (%)	80 min.	83 min.	78-83	76 min.	80 min.	82 min.
Free Fatty Matter (%)	10 max.	10 max.	12-14	4 max.	10 max.	10 max.
Sodium Chloride (%)	0.01 max.	0.8 max.	—	2%	0.8 max.	0.8 max.
pH, % sol'n.	5-7 (5%)	6.5-8 (10%)	4.7-6.0 (10%)	7.5 ± .5 (1% sol'n.)	6.5-8.0 (5%)	
Water (%)	1 max.	2 max.	0.3-0.8	1 max.	2 max.	
Iron (as Fe)		25 ppm				25 ppm
Color (5%) APHA	50 max.	50 max.	15-40		50 max.	
% Sodium Sulfate		0.25% max.				
Arsenic (As)						3 ppm max.
Lead (Pb)						20 ppm max.
Sodium Carbonate		0.1% max.				

(1) Compendium from all vendors (each vendor has specifications taken from this list).

nut fatty acid of choice is 338. Vendor D is using a fatty acid which has a different distribution and most likely contains less C_8 fatty acids. The CTFA specification actually provides a fatty acid distribution which contains no C_8 fraction. The reason has not been determined. Obviously, the alkyl distribution will determine the average molecular weight and the claimed activity of the product. For example, if the 341 and 345 MW figures are adjusted to 338, then the activities would be 81.3% and 74.5%, respectively. As we shall see, a close analysis of the alkyl distribution and a calculation of the "real" average MW will afford a more meaningful analysis of the percent actives.

The second point to be understood in comparing these specifications is that the percentages for the various ingredients in SCI do not add up to 100%. For example, SCI from Vendor A, prepared by the direct route, exhibits the following typical analysis:

Actives (MW 338):	83.1%
Free Fatty Matter:	5.7%
Moisture:	0.4%
Total:	89.2%

None of the vendors has a specification for unreacted sodium isethionate because an analysis for this ingredient is difficult to perform. However, an analysis by R. Otterson, manager of Jordan's analytical department, based on HPLC, shows the above preparation to have 3.9% unreacted sodium isethionate and 1.4% of an unknown ionic species (most likely derived from sodium isethionate). Including these values, the analysis accounts for 94.5%. This now leaves 5.5%

Dr. Robert B. Login

unexplained. Possible candidates could be the low or high end isethionate esters because they contribute approximately this level of material. Preparation in the laboratory of a homolog from pure myristic acid afforded the following analysis:

Activity (MW 358):	88.2%
Free Fatty Matter:	8.9%
Moisture:	0.2%
Sodium Isethionate:	2.1%
Unknown Ionic:	0.9%
Total:	100.3%

The analysis for actives is based on the classical Epton (Methylene Blue) two-phase titration. The possibility that the lowest molecular weight homolog prepared from the Caprylic acid fraction doesn't titrate proved to be false. The literature reports that C_6 based anionics do not titrate whereas C_8 do. Therefore, it is likely that the problem is the response of the C_{16}-C_{18} fraction or interferences caused by the unreacted fatty acids. Simply comparing SCI on the basis of actives alone is incorrect. SCI must be evaluated on the total analysis if a true picture of quality is to be correctly assessed.

The free fatty matter specification takes into account the titratable fatty acids and extractable ester. It is an extraction procedure and is reported as a percentage. Both the level of material and the breakdown between the fatty acids and esters are important. Obviously, too much coconut fatty acid is a negative for two reasons: Free fatty acids, especially the low ends, are known to cause irritation; and fatty esters are associated with defoaming and poor soap bar mix characteristics. Therefore, high levels of free fatty matter are considered to be a negative.

An analysis of the fatty acids associated with SCI, both free and esterified, shows some differences from one manufacturer to another and is somewhat altered from the original hydrogenated fatty acids, especially with regard to those products formed by the direct reaction. It would seem reasonable that the acid chloride route would not distill over the light ends as would be expected during the high temperature direct reaction. *Table 3* shows the comparison of grades A, B and C for fatty acid distribution.

When comparing the different grades of SCI, it would be apparent that Product B was prepared by the acid chloride route while Products A and C were made by the direct reac-

TABLE 3							
Free and Bound Fatty Acid Distributions (1)							
	Product A		Product B		Product C		Patent (2)
Fatty Acid	% in Free	% in Product	F	P	F	P	Example (P)
C8	4.3	4.5	3.0	6.1	2.6	4.3	3.0
C10	4.7	5.4	4.9	5.8	4.2	4.9	5.0
C12	46.6	48.8	50.0	47.3	49.7	47.3	45.0
C14	20.6	20.2	19.0	18.2	22.5	21.7	18.0
C16	10.6	10.3	9.4	9.9	11.8	10.9	14.0
C18	9.5	6.7	8.5	7.5	9.2	8.6	10.0
C18-1	3.7	4.1	5.1	5.2	-0-	2.4	5.0

(1) GIC analysis of corresponding methyl esters
(2) US 3,879,309 (L. Gatti and R. G. Matthaei; Lever, 1975)

tion as evidenced by the level of C_8 fatty acid and the salt content. Product B, with significantly higher C_8 ester, is expected to show higher actives than Products A or C because the molecular weight of the C_8 ester is significantly lower than the 338 average molecular weight used to calculate activity. Therefore, a one percent increase in the C_8 ester would increase the actives by (338/274 [MW of C_8 ester]) 1.23%. Product B can claim higher actives, but this simply relates to the higher C_8 ester level. Does C_8 ester do anything for the syndet or combo bar formulation? Once again, this analysis shows that the uninformed comparison of actives alone is not indicative of performance. *Table 4* confirms this opinion based on a comparison of Ross-Miles foam heights.

Vendor D's specifications are so far removed from the others that it is difficult to compare. The use of SCI from Vendor D would require significant adjustments in the soap bar formulations such as those proposed by Lever Brothers' patents. Therefore, it might not be considered at all by the formulator.

Necessity of Free Sodium Isethionate

The actual amount of unreacted sodium isethionate is very important to the processing of combination and syndet bar formulations. Its level affects the rheology of the syndet/combo bar mix and plodding characteristics. Haass and Lamberti (U.S. Patent No. 3,376,229; Lever Bros., 1968) clearly spell out the necessity for free sodium isethionate: "In accordance with the present invention, it has been found that the presence of free isethionate will noticeably improve the hardness and processing characteristics of detergent bars . . . As little as about 2.5% of free isethionates in the detergent bar (based on the finished weight thereof) will provide a substantial improvement in the plodding characteristics . . . Most commercial preparations of the isethionate esters will contain some small amount of free isethionates, and this should be taken into consideration as contributing to improved plodding characteristics."

TABLE 4		
Ross—Miles Foam		
	Foam Height (MM)	
Product Tested	Initial	5 Minutes
A	133	133
B	132	132
C	120	120

All products were tested at a concentration of 0.05% solids.

Our analysis indicates that Product A contains an average 3-4%; Product B—2.5%; and Product C—1-1.5%. Product A happens to have a more appropriate level of free sodium isethionate and may not require the addition of more into the formulation. If the free sodium isethionate level is too low the formulator is faced with the necessity of adding more, either as a powder or working off the water that comes with the 57% solution. This may not be a problem; however, it shows how an overall analysis of SCI can impinge on performance even though not addressed in current specifications.

Sodium chloride levels also vary between brands of SCI. Those made by the direct process have essentially none, while those made from the acid chloride route have significant quantities. References U.S. Patent Nos. 2,923,724 and 3,004,049 (Anderson, Schenck; GAF) both report the adverse effect of salt. For example, Schenck states, "In addition, a considerable quantity of salt is concurrently produced (by the acid chloride route—author's note) which is highly undesirable in many uses, particularly when the resulting isethionic acid ester is employed in detergent and built soap formulations. Further, the salt in such formulations imparts thereto an unduly high hygroscopicity, and its removal is expensive." Whether or not the syndet/combo bar formulator will have a problem with higher levels of salt is speculative; it is nonetheless a real concern. Having a product without very much salt would be an advantage in that it could always be added if needed.

The pH specification also exhibits variations according to the method of manufacture. Those products prepared by the acid chloride route have higher pH ranges than those prepared by the direct route. The direct route producers do not ordinarily adjust pH but accept it as is. For example, Vendor C's product, because of significantly higher free fatty acid, exhibits a lower pH specification. The soap bar formulator, in order to take advantage of SCI's stability at low pH's, is faced with having to adjust the pH of his formulations down when higher pH products are used. Products made by the direct process, however, require little or no adjustment.

In addition, Geitz reports that the ideal pH for the Lever type product is 6.8 to 7.2. "In the presence of the unneutralized coconut oil fatty acids in a sufficient amount, and at a pH of 6 to 6.5, the water penetration of the nonsoap bar of the invention is superior to soap with respect to overnight sloppiness due to water penetration. Increasing the pH tends to lessen the resistance of the bar to water penetration, but at pH's up to 7.2, resistance to water penetration still is satisfactory."

Turning to other specifications in Table 2, we may com-

(Continued on page 88)

TABLE 3							
Free and Bound Fatty Acid Distributions (1)							
	Product A		**Product B**		**Product C**		**Patent (2)**
Fatty Acid	**% in Free**	**% in Product**	**F**	**P**	**F**	**P**	**Example (P)**
C8	4.3	4.5	3.0	6.1	2.6	4.3	3.0
C10	4.7	5.4	4.9	5.8	4.2	4.9	5.0
C12	46.6	48.8	50.0	47.3	49.7	47.3	45.0
C14	20.6	20.2	19.0	18.2	22.5	21.7	18.0
C16	10.6	10.3	9.4	9.9	11.8	10.9	14.0
C18	9.5	6.7	8.5	7.5	9.2	8.6	10.0
C18-1	3.7	4.1	5.1	5.2	-0-	2.4	5.0

(1) GIC analysis of corresponding methyl esters
(2) US 3,879,309 (L. Gatti and R. G. Matthaei; Lever, 1975)

tion as evidenced by the level of C_8 fatty acid and the salt content. Product B, with significantly higher C_8 ester, is expected to show higher actives than Products A or C because the molecular weight of the C_8 ester is significantly lower than the 338 average molecular weight used to calculate activity. Therefore, a one percent increase in the C_8 ester would increase the actives by (338/274 [MW of C_8 ester]) 1.23%. Product B can claim higher actives, but this simply relates to the higher C_8 ester level. Does C_8 ester do anything for the syndet or combo bar formulation? Once again, this analysis shows that the uninformed comparison of actives alone is not indicative of performance. *Table 4* confirms this opinion based on a comparison of Ross-Miles foam heights.

Vendor D's specifications are so far removed from the others that it is difficult to compare. The use of SCI from Vendor D would require significant adjustments in the soap bar formulations such as those proposed by Lever Brothers' patents. Therefore, it might not be considered at all by the formulator.

Necessity of Free Sodium Isethionate

The actual amount of unreacted sodium isethionate is very important to the processing of combination and syndet bar formulations. Its level affects the rheology of the syndet/combo bar mix and plodding characteristics. Haass and Lamberti (U.S. Patent No. 3,376,229; Lever Bros., 1968) clearly spell out the necessity for free sodium isethionate: "In accordance with the present invention, it has been found that the presence of free isethionate will noticeably improve the hardness and processing characteristics of detergent bars . . . As little as about 2.5% of free isethionates in the detergent bar (based on the finished weight thereof) will provide a substantial improvement in the plodding characteristics . . . Most commercial preparations of the isethionate esters will contain some small amount of free isethionates, and this should be taken into consideration as contributing to improved plodding characteristics."

TABLE 4		
Ross—Miles Foam		
	Foam Height (MM)	
Product Tested	**Initial**	**5 Minutes**
A	133	133
B	132	132
C	120	120

All products were tested at a concentration of 0.05% solids.

Our analysis indicates that Product A contains an average 3-4%; Product B—2.5%; and Product C—1-1.5%. Product A happens to have a more appropriate level of free sodium isethionate and may not require the addition of more into the formulation. If the free sodium isethionate level is too low the formulator is faced with the necessity of adding more, either as a powder or working off the water that comes with the 57% solution. This may not be a problem; however, it shows how an overall analysis of SCI can impinge on performance even though not addressed in current specifications.

Sodium chloride levels also vary between brands of SCI. Those made by the direct process have essentially none, while those made from the acid chloride route have significant quantities. References U.S. Patent Nos. 2,923,724 and 3,004,049 (Anderson, Schenck; GAF) both report the adverse effect of salt. For example, Schenck states, "In addition, a considerable quantity of salt is concurrently produced (by the acid chloride route—author's note) which is highly undesirable in many uses, particularly when the resulting isethionic acid ester is employed in detergent and built soap formulations. Further, the salt in such formulations imparts thereto an unduly high hygroscopicity, and its removal is expensive." Whether or not the syndet/combo bar formulator will have a problem with higher levels of salt is speculative; it is nonetheless a real concern. Having a product without very much salt would be an advantage in that it could always be added if needed.

The pH specification also exhibits variations according to the method of manufacture. Those products prepared by the acid chloride route have higher pH ranges than those prepared by the direct route. The direct route producers do not ordinarily adjust pH but accept it as is. For example, Vendor C's product, because of significantly higher free fatty acid, exhibits a lower pH specification. The soap bar formulator, in order to take advantage of SCI's stability at low pH's, is faced with having to adjust the pH of his formulations down when higher pH products are used. Products made by the direct process, however, require little or no adjustment.

In addition, Geitz reports that the ideal pH for the Lever type product is 6.8 to 7.2. "In the presence of the unneutralized coconut oil fatty acids in a sufficient amount, and at a pH of 6 to 6.5, the water penetration of the nonsoap bar of the invention is superior to soap with respect to overnight sloppiness due to water penetration. Increasing the pH tends to lessen the resistance of the bar to water penetration, but at pH's up to 7.2, resistance to water penetration still is satisfactory."

Turning to other specifications in Table 2, we may com-

(Continued on page 88)

Sodium Cocoyl Isethionate

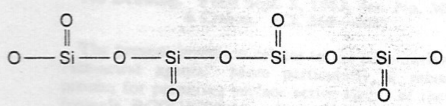
(Continued from page 60)

ment that color, like foreign impurities, must be kept to a minimum. Water can contribute plasticity to the soap bar formulations and should also be kept to a minimum. (The acid chloride route, because of the necessity to neutralize hydrochloric acid, appears to require higher water specification.) Iron, arsenic and lead are contaminents brought in by the raw materials or materials of construction used in the process. The acid chloride route requires more corrosion resistant materials of construction such as lead lined equipment. Sodium sulfate is a contaminent in the sodium isethionate used to make the SCI, while sodium carbonate is a residual base used to neutralize the trace of remaining hydrochloric acid generated during the process. ■

Silica Derivatives

(Continued from page 72)

terials. Here again the phenomenon of polymerization is encountered. The structure can be pictured:



The exact molecular weight or degree of polymerization depends on the conditions of manufacture. In addition, the terminal —O group(s) can have a hydrogen atom attached. This radical can react with chlorosilanes, mentioned above, to produce anti-foams or by hydrogen bonding with reactive or semi-reactive radicals. This latter phenomenon is used to thicken both aqueous and non-aqueous liquids.

The fumed silicas are treated to make them either hydrophobic or hydrophyllic. The manufacturer, therefore, has a choice of particle size, bulk density, reactivity and water repelling properties.

Allied with, but not identical to these fine silicas, are finely divided metallic silicates, aluminium, calcium and magnesium, which have many of the properties of the silicas except the reactivity, which can sometimes be a disadvantage.

It can thus be seen that the uses for silicon compounds are extremely varied. The alchemists of yore spent their lives, with no success, in attempting to convert base metals into gold. Modern technology has succeeded in converting base minerals into extremely useful products! ■

References

1. E.G. Rochow, Modern Chemistry for the Engineer and Scientist, (G. Ross Robertson Editor), p 212, McGraw-Hill.
2. A. Davidsohn & B. Milwidsky, Synthetic Detergents, 6th Edition, p 139, George Godwin, London.
3. G.C. Schweiker, J Am Oil Chem Soc, 55, 38, (1978).
4. H. Weldes, Soap, 72, (May 1972).
5. Y. Sugahara, et al, US Patent 4,238,346, Dec. 9, 1980.