C-21 Dicarboxylic Acids in Soap and Detergent Applications

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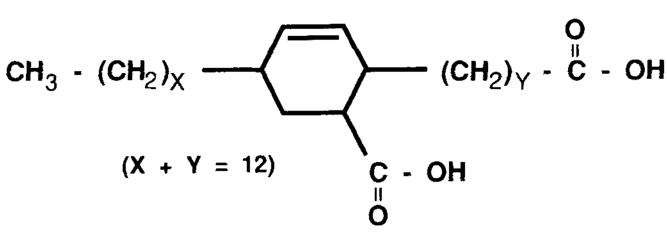
A unique polycarboxylic acid, 5(6)-carboxy-4-hexyl-2-cyclohexene-1-octanoic acid, has been available commercially for over 15 years. A new high-purity (>97%), light-color version of the C-21 dicarboxylic acid has been developed recently. Soaps of the C-21 dicarboxylic acid can be used as hydrotropes to increase the solubility of nonionic surfactants in aqueous solutions containing builders and/or anionic surfactants. Since these soaps are anionic fatty acid derivatives, they reduce the surface tensions of formulations, thus improving detergency. The nontoxic and biodegradable nature of this dicarboxylic acid makes it an attractive formulation component. This paper outlines application evaluations of the soaps prepared from the C-21 dicarboxylic acids. These evaluations demonstrate how the soaps interact with nonionic surfactants or pine oil to provide clear formulations, how they wet cotton skeins in neutral to highly alkaline solutions, and how they inhibit gel formation when preparing high-solids fatty acid soap solutions. Furthermore, the preparation and characterization of the soaps of the C-21 dicarboxylic acid products are discussed. Mass-balance equations describe the preparation of aqueous soap solutions at any given concentration. Characterization of the resulting soap solutions includes acid number, pH, color, color stability, foam stability, surface tension as a function of concentration, and hard-water compatibility.

KEY WORDS: **Biodegradable, C-21 dicarboxylic acid, concentrates, detergent, diacid, hydrotrope, nontoxic, soap.**

Westvaco Corporation has been manufacturing an industrial-grade C-21 dicarboxylic acid for use in soap and detergent applications for a number of years. This material, 5(6)-carboxy-4-hexyl-2-cyclohexene-1-octanoic acid, known commercially as WESTVACO DIACID® 1550 C-21 dicarboxylic acid, is prepared by the Diels-Alder cycloaddition of acrylic acid with the linoleic acid in tall oil fatty acids. The structure of the C-21 dicarboxylic acid is as follows:



SCHEME 1

The product has been used in liquid laundry detergents, liquid dish detergents, hard-surface cleaners, pine cleaners, and other soap and detergent formulations.

Westvaco recently developed a high-purity (>97%), light-color version of the C-21 dicarboxylic acid for specialty detergent and personal-care applications. This developmental diacid product is referred to as D-1595. A comparison of the two products is given in Table 1. Both products are biodegradable and nontoxic, making them attractive formulation components for an industry that is increasing its efforts to sell environmentally friendly products (1).

TABLE 1

Composition of C-21 Dicarboxylic Acid Products

	DIACID 1550	D-1595
Monomer fatty acid	20–22%	1–2%
C-36 dimer fatty acid	10%	≤ 1%
Color (Gardner units)	7–8	3–4
Acid number	270–275	305–310
Saponification value	300–305	315–320

EXPERIMENTAL PROCEDURES

The soaps of the C-21 dicarboxylic acids are prepared by adding the C-21 dicarboxylic acid to an appropriate amount of alkali in water. In order to determine the amounts of reagents necessary for preparing the soaps, three mass-balance equations (Equations [1], [2], and [3]) are used. The equations allow preparation of a soap at a concentration and acid number close to a desired level by determining the amounts of fatty acid, alkali, and water needed for the procedure. Strong bases must be used in order for these equations to be valid, otherwise the potential for incomplete deprotonation exists. When a concentration is targeted, the measured concentration is usually slightly lower than the target value, due to the water generated during the neutralization.

Grams alkali necessary to neutralize 1000 grams diacid:

$$\text{grams alkali} = \frac{(\text{acid number}) \times (\text{equivalent wt. base}/56.1)}{\text{activity of alkali}} \qquad [1]$$

Total mass of reaction mixture:

$$\text{Total mass} = \frac{(\text{grams alkali}) \times (\%\ \text{cation}) + \text{grams diacid}}{\text{desired activity of soap}} \qquad [2]$$

Grams of water to dilute reaction mixture:

$$\text{grams water} = \text{total mass} - \text{grams alkali} - \text{grams diacid} \qquad [3]$$

RESULTS AND DISCUSSION

This work focuses first on the application evaluation and then on the characterization of soaps prepared from the

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two diacid products from a detergent formulator's perspective. When possible, comparisons are made with hydrotropes commonly used in the industry. Results demonstrate that on a weight basis, the high-purity D-1595 has superior hydrotroping properties when compared with sodium xylene sulfonate, phosphate esters, diphenyl ether sulfonates, and alkyl naphthalene sulfonates. On a cost performance basis, DIACID 1550 would be the product of choice in most detergent applications considered.

The most notable property of the diacid is its ability to increase the solubility of nonionic surfactants in aqueous solutions containing builders and/or anionic surfactants. Coupling power was determined by several methods, including a solubility comparison of several common nonionic surfactants, a determination of the minimum amount of hydrotrope needed to clarify a typical pine oil disinfectant cleaner, and the Draves wetting efficiency of a nonionic-hydrotrope combination at increasing levels of alkali concentrations. Also of interest is the finding that the C-21 dicarboxylic acids can be converted to high-solids soap solutions. A description of the commercial hydrotropes used for comparison purposes can be found in Table 2.

Solubility determination. The solubility of nonionic surfactants in water is affected by the presence of hydrotropes. As the hydrotrope efficiency increases, the amount necessary to clear the nonionic solution decreases. In this experiment, all of the hydrotropes were titrated onto a series of nonionic surfactants in the presence of builders, and the hydrotrope volume needed to clear the solutions was determined. As shown in Table 3, the potassium soap of D-1595 is most effective at clearing aqueous solutions of nonionic surfactants. However, on a cost-performance basis, the potassium soap of DIACID 1550 would be the preferred hydrotrope of the six compared in this paper.

Hydrotrope requirements for a typical pine oil disinfectant cleaner. Experiments were done to determine the minimum amount of hydrotrope needed to produce a clear pine oil disinfectant formulation. The formulation and the break-point hydrotrope concentrations for diacid soaps and standard commercial hydrotropes are shown in Figure 1. Both diacid products are more efficient at producing clear pine oil disinfectant formulations than the commercial standards in this study. Similar trends were observed in other detergent formulations, including liquid laundry, hard-surface, and metal-cleaning formulations.

Draves wetting efficiency. Nonionic surfactants are typically insoluble in highly alkaline aqueous media unless efficient hydrotropes are added. With a given surfactant-hydrotrope combination, the hydroxide concentration where phase separation takes place is a measure of the hydrotrope efficiency. In this experiment, Draves wetting speeds were used to determine the hydroxide concentrations where the nonionic fails to function as a surfactant

TABLE 2

Description of Commercially Available Hydrotropes

Chemical classification	Trade name	Source
Sodium xylene sulfonate	SXS	Aldrich Chemical Co.
Phosphate ester	TRITON H-66	Union Carbide
Alkyl naphthalene sulfonate	PETRO BA	DeSoto Chemicals
Diphenyl ether sulfonate	DOWFAX 2A-1	Dow Chemical Co.

TABLE 3

Solubility Determinations of Aqueous Nonionic Surfactants

	Nonionic				
Hydrotrope	Ipepal CO-530	Plurafac RA-40	Tetronic 701	Tergitol 15-S-7	Neodol 23-6.6
D-1595 (potassium soap)	1.1[a]	0.6	0.4	0.3	0.4
DIACID 1550 (potassium soap)	1.4	0.8	0.8	0.9	1.5
Sodium xylene sulfonate	3.3	4.4	4.5	1.3	1.4
Diphenyl ether sulfonate (sodium salt)	2.2	1.7	0.9	0.5	0.8
Phosphate ester (potassium salt)	2.3	4.5	3.0	0.6	0.9
Alkyl naphthalene sulfonate (sodium salt)	2.2	2.5	1.6	2.2	1.8

[a]Volume (in mL) of hydrotrope (100% active) required to produce a clear nonionic solution (2%) in water containing sodium carbonate (3.2%), sodium tripolyphosphate (2.4%), and sodium silicate (5.6%) at 25°C.

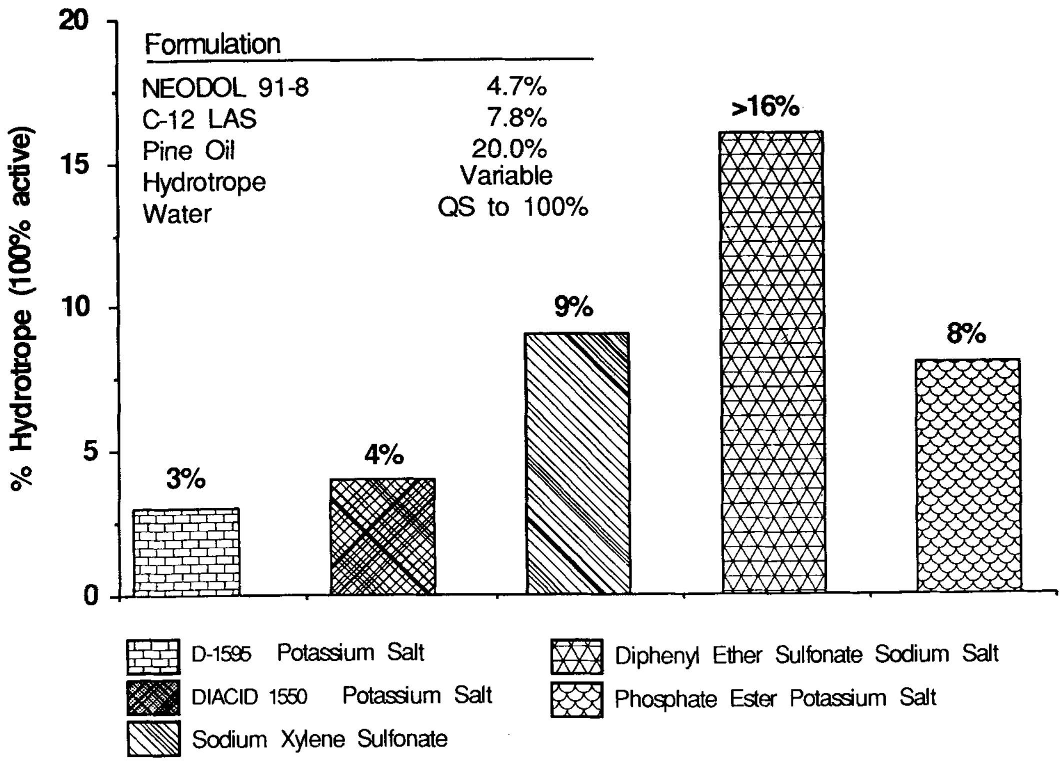

FIG. 1. Diacid soaps produce clear pine oil formulations at lower concentrations than standard hydrotropes.

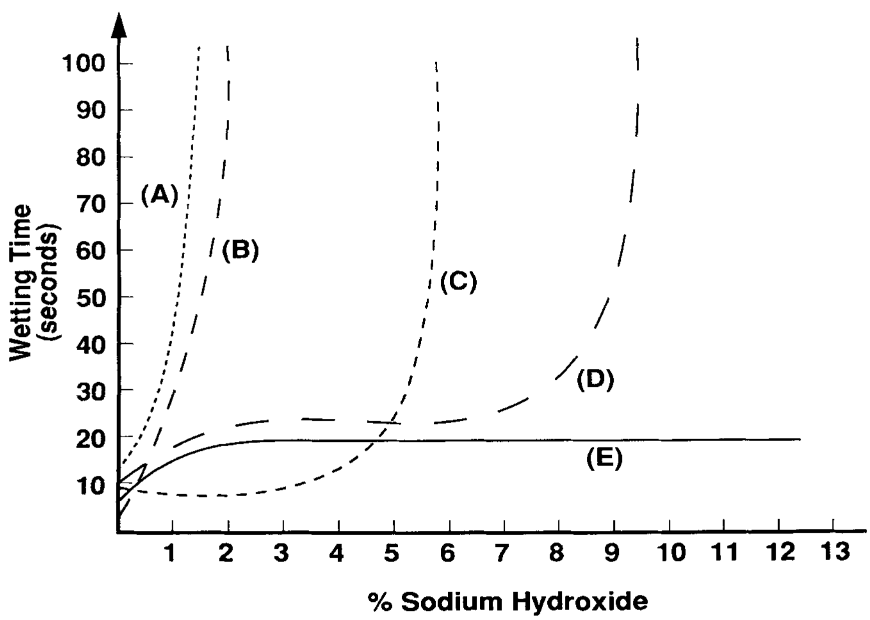

FIG. 2. Hydrotrope efficiencies by Draves wetting speeds at 49°C. Surfactant conc., 0.1%; nonylphenol-9EO/hydrotrope ratio, 1:1. Hydrotrope used: A, SXS; B, nonionic only @ 0.1%; C, phosphate ester potassium salt; D, diphenyl ether sulfonate sodium salt; E, DIACID 1550 sodium salt.

(2). The Draves wetting times were determined for aqueous solutions of Triton N-101/hydrotrope combinations with increasing amounts of sodium hydroxide (1% increments) until the cotton skeins would no longer wet. Triton N-101 is a nonylphenol ethoxylate nonionic surfactant. The results, illustrated in Figure 2, show that the diacid soaps perform better than the commercial standards in the highly alkaline detergent solutions. This experiment is a good comparison of hydrotrope efficiencies. It is indicative of good performance in metal-cleaning or textile-scouring applications.

High-solids soap solutions can be prepared with C-21 dicarboxylic acids. Concentrated formulations are becoming very popular with soap and detergent manufacturers, and several companies have introduced concentrates. The advantages for selling concentrates include lower packaging costs and lower transportation costs. Consumers find concentrated products more convenient because a single container lasts longer in the home.

The solubility of a fatty acid soap in water is dependent on the backbone of the fatty acid as well as the counterion. For example, the maximum concentration for the potassium soap of oleic acid is 20%, and 36% for coconut fatty acid (3). The soaps of the C-21 dicarboxylic acid are exceptionally soluble in water. With an arbitrary maximum viscosity of 2000 cps, the potassium soap of DIACID 1550 can be prepared at 68% solids, while D-1595 can be prepared at 73% solids (Fig. 3). In general, the viscosity as a function of counterion at a given solids content increases in the following order: triethanolammonium (TEA^+) < K^+ < NH_4^+ < Na^+. Also, our results demonstrate that higher-solids soap solutions can be made from the high-purity diacid product for the four cations. Interestingly, sodium xylene sulfonate (SXS) is a high-viscosity paste above 53% solids.

Diacid soaps also allow the preparation of other fatty acid soaps at concentrations not normally attainable without gelation. For example, by preparing a 90% oleic acid/10% diacid blend with either C-21 dicarboxylic acid product, aqueous soap solutions with close to a 50% increase in maximum solids can be prepared (Fig. 3). A 75% increase in solids could be achieved when a small amount of DIACID 1550 is blended with tall oil fatty acid (TOFA). Even though the soaps of TOFA usually gel at 22% solids, soap solutions were prepared at 38.5% solids with a 20% blend of diacid in the fatty acid (Fig. 4). Slightly larger increases in solids were obtained when the high-purity D-1595 was used in the formulations instead of the DIACID 1550. Figure 5 shows the viscosity at different soap concentrations for blends of TOFA and D-1595.

The ability to produce high-solids soap solutions is postulated to result from the large interfacial surface area required by the two polar head groups on the C-21 dicarboxylic acid soap (4–7). The diacid molecules interrupt surface packing, interfere with liquid crystal structures, and enhance micelle formation in concentrated surfactant solutions.

C-21 dicarboxylic acid in liquid laundry formations. For years, DIACID 1550 has been used in liquid laundry formulations. We have made comparisons of typical liquid laundry formulations prepared with both dicarboxylic acid products as well as with sodium xylene sulfonate, a hydrotrope commonly used for this purpose. While only small differences were noticed in the formulation stability, the detergent prepared with DIACID 1550 soaps cleaned better than the others. Other advantages for using the dicarboxylic acid have been observed. By pre-blending the dicarboxylic acid soaps with optical brighteners, the time required for complete dissolution of the solid particles in the formulation is reduced, potentially decreasing cycle times when formulating batches. Also, the loading of the optical brightener on the fabric is enhanced when DIACID 1550 is used. These results will be discussed in greater detail in a future publication.

Acid number and pH of soap solutions. The soaps made with sodium and potassium hydroxide were completely

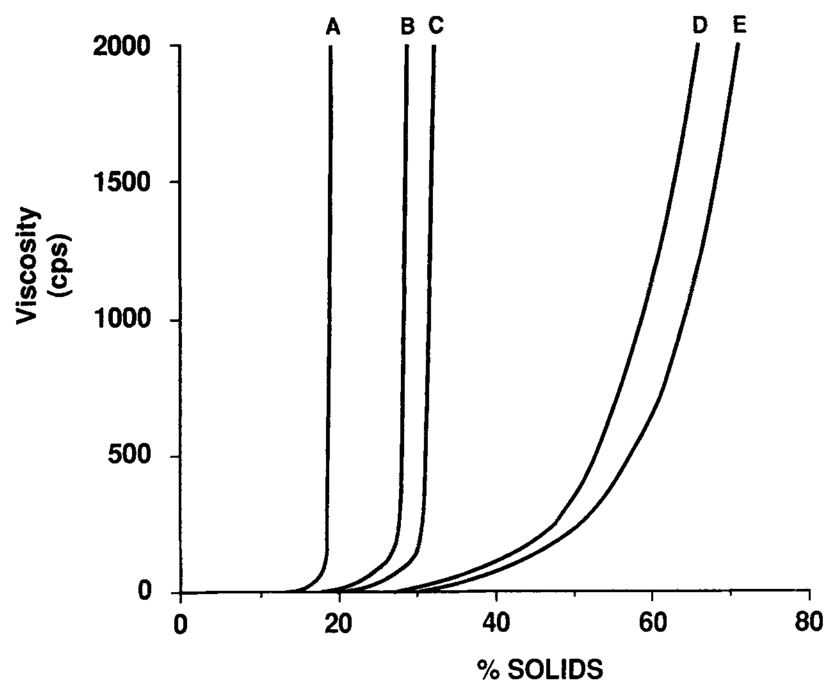

FIG. 3. Viscosities *vs.* solids for diacid and diacid/oleic acid blends as potassium soaps. A, oleic acid; B, oleic acid/DIACID 1550 (9:1); C, oleic acid/D-1595 (9:1); D, DIACID 1550; E, D-1595.

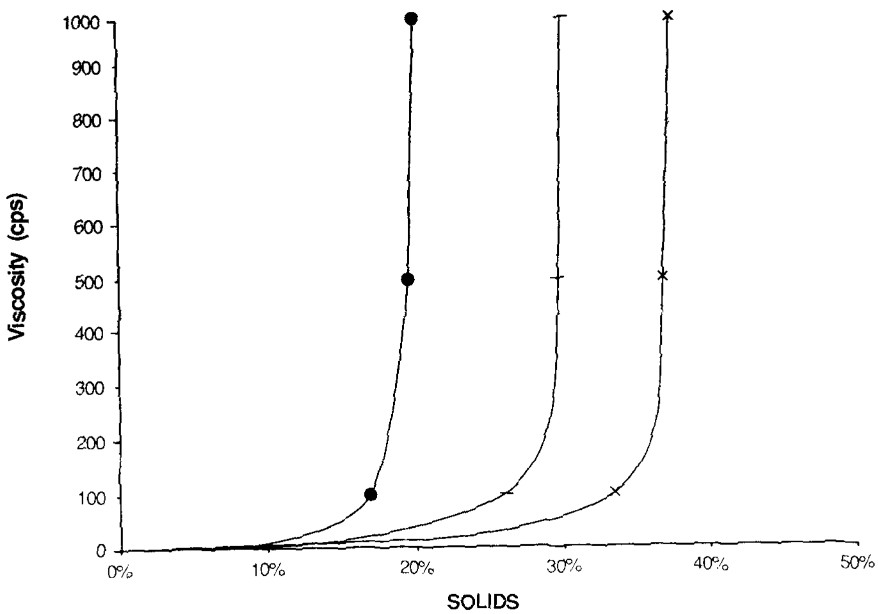

FIG. 4. Viscosity *vs.* solids for soaps prepared from tall oil fatty acid/DIACID 1550 blends as potassium soaps. Closed circle, TOFA/no DIACID; dash, TOFA/10% DIACID; x, TOFA/20% DIACID.

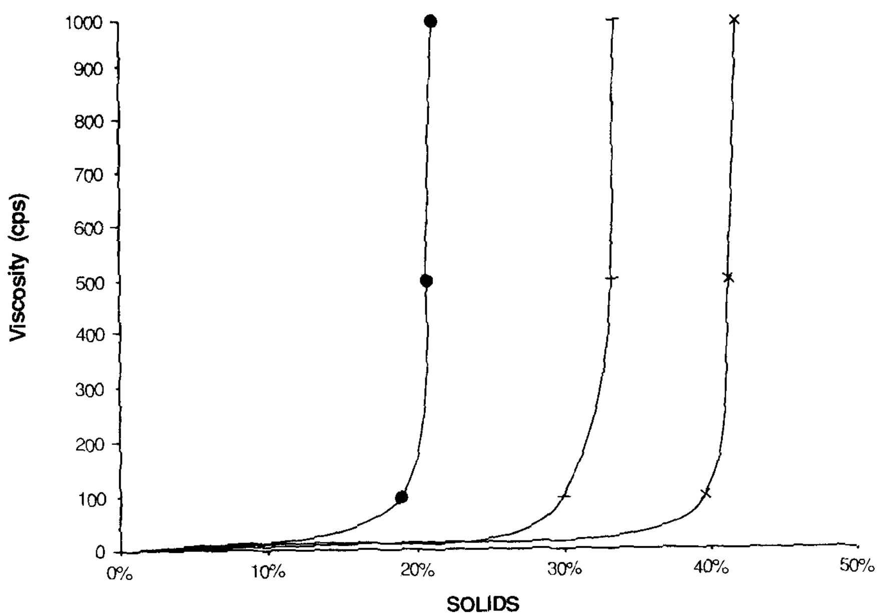

FIG. 5. Viscosity *vs.* solids for soaps prepared from tall oil fatty acid/D-1595 blends as potassium soaps. Legends as in Figure 4.

neutralized to an acid number of zero, while the soaps from ammonium hydroxide and triethanolamine were partially neutralized to an acid number ranging from 65 to 110 (Table 4). This reflects differences in the base strengths between alkali metal and organic bases. The pH of the soap solutions also illustrate the effect of the base strength. With strong alkali, complete deprotonation occurs, and excess alkali can raise the pH above 10.5. With the weaker alkali, complete deprotonation does not occur, and the pH remains below 9.0. Below pH 9.0, the diacid exists in the half-soap/half-acid form (3).

Color and color stability determinations. The soaps of the high-purity D-1595 averaged four Gardner units lighter in color for the strong alkali and two Gardner

TABLE 4

Characterization of Polycarboxylic Acid Soaps

	DIACID 1550	D-1595
Sodium soaps		
Solids (%)	37.4	37.1
Acid number	0	0
pH (10% soln.)	10.5	11.0
Initial color, Gardner units	8	4
Shelf color stability, Gardner units	8	4
Potassium soaps		
Solids (%)	35.0	34.5
Acid number	0	0
pH (10% soln.)	10.9	12.0
Initial color, Gardner units	8	4
Shelf color stability, Gardner units	8	4
Ammonium soaps		
Solids (%)	36.5	36.4
Acid number	94.1	106
pH (10% soln.)	7.8	7.5
Initial color, Gardner units	7	5
Shelf color stability, Gardner units	12	10
Triethanolammonium (TEA) soaps		
Solids (%)	41.1	41.2
Acid number	65.5	72.0
pH (10% soln.)	7.7	7.6
Initial color, Gardner units	5	3
Shelf color stability, Gardner units	8	6

TABLE 5

Accelerated Color Stability of Diacid Soaps

	Gardner color over time at 50°C			
Sample	Initial	1 Week	3 Weeks	6 Weeks
D-1595				
Sodium	4	5	5	8
Potassium	4	6	7	11
Ammonium	5	8	14	16
TEA	3	8	12	13
DIACID 1550				
Sodium	8	11	11	13
Potassium	8	11	12	15
Ammonium	7	14	15	18
TEA	5	12	14	17

units lighter in color for the weak alkali than the same soaps from the industrial-grade DIACID 1550 (Table 4). The triethanolamine soaps were initially the lightest in color in both instances.

Color stability was determined by two procedures. In the first test, long-term or shelf-color stability on the lab bench at ambient temperature was noted over three months. The soaps neutralized with amines were less color stable than the other soaps. The sodium and potassium soaps remained at the original color, while the ammonium and TEA soaps darkened between three and five Gardner units (Table 4).

The second method of determining color stability was a high-temperature or accelerated color stability test. Here, the soaps were placed in an oven at 50°C for six weeks. The Gardner color was measured at one-week intervals; the results after the first, third, and sixth week are given in Table 5. Again, the sodium and potassium soaps were more color stable than the ammonium or the TEA soaps.

Surface tension. One of the fundamental qualities for surfactants is the ability to reduce the normally high surface tension of water. The surface tensions were measured for the potassium salts of the two diacid products. Comparisons were made with soaps of a tall oil fatty acid, sometimes used as a primary anionic surfactant, and with sodium xylene sulfonate (SXS), a standard commercial hydrotrope. The results are illustrated in Figure 6, where the surface tension is plotted as a function of surfactant concentration.

The TOFA soap was the most effective at reducing the surface tension of water, followed by the DIACID 1550 soap, then the D-1595 soap, and finally the SXS. The monomeric fatty acid present in the DIACID 1550 ac-

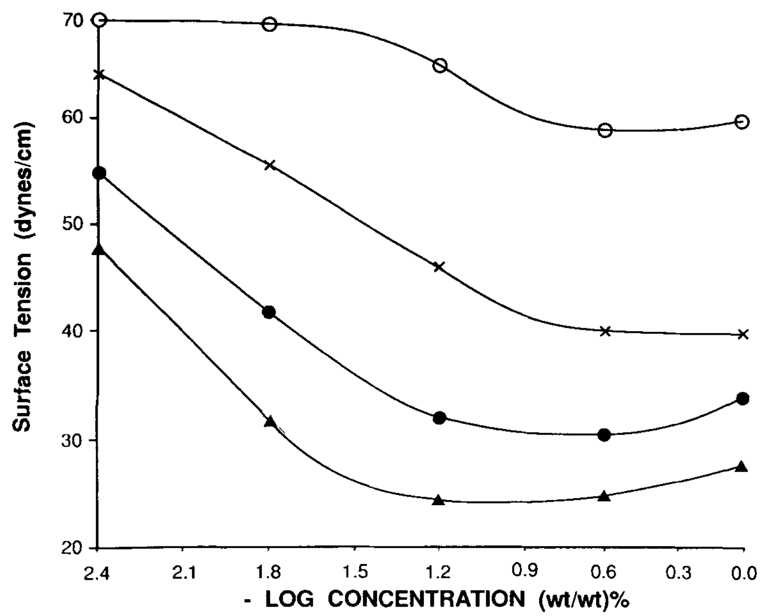

FIG. 6. Surface tension measurements for diacid potassium soaps. Open circle, SXS; x, D-1595; closed circle, DIACID 1550; triangle, TOFA.

counts for the improved surface tension reductions over the higher-purity D-1595 product. Even though the soaps of TOFA are better at reducing the surface tension in dilute solutions, at the normal use concentrations for hydrotropes (*ca.* 4–8%), the diacids are almost as effective as the monomeric fatty acid soaps. The diacid soaps would not be considered primary anionic surfactants, but they contribute to surface tension reductions and help improve cleaning efficiency as compared to formulations containing the standard commercial hydrotropes, such as sodium xylene sulfonate.

Ross-Miles foaming properties (8). In certain applications, such as laundry detergents and liquid cleaners, formulations with a high, stable foam are desirable; while in others, such as metal-cleaning or machine-dishwashing formulations, low, unstable foams are sought. Ross-Miles foaming tests demonstrate that the foaming properties of the high-purity D-1595 soaps are similar to the foaming properties of the DIACID 1550 soaps (*i.e.*, high and stable). While the foam levels are not high enough for the diacid soaps to be considered as a foam-boosting agent, they should increase foam levels in detergents. SXS produces no foam at all. A summary of the foaming results for the potassium soaps in deionized water at pH 10.5 is illustrated in Table 6.

Hard-water compatibility. Resistance to flocculation in the presence of hard-metal ions, such as Ca^{+2} and Mg^{+2}, is an important consideration when choosing formulation components. The procedure used to measure the hard-water compatibility of the diacid soaps involves titrating the hard-water solution (300 or 500 ppm) into a given volume of soap solution (1%, w/w) until cloudiness appears. Higher amounts of hard-water titrated into the solution before a cloudy appearance indicates greater compatibility with hard-metal ions. The results, illustrated in Table 7, show only minor differences between the two diacid samples. D-1595 is slightly more sensitive to hard water than DIACID 1550, presumably due to the regular fatty acids present in the latter. More significant differences are noticed with different counterions. Like the coconut fatty acid soaps, the sodium and potassium soaps of diacid are sensitive to the presence of hard-metal ions. The nitrogen-containing soaps, on the other hand, are much more tolerable to hard-water. The increased hard-water compatibility probably results from the lower pH of the soaps prepared with a weak base. If a formulation must perform in hard-water areas, excessive amounts of diacid would have to be avoided.

We have demonstrated that soaps of WESTVACO DIACID® 1550 and D-1595 can be used as hydrotropes to increase the solubility of nonionic surfactants in aqueous solutions containing builders and/or anionic surfactants. In general, our results demonstrate that when compared on a weight basis, the high-purity D-1595 has superior hydrotroping properties compared with sodium xylene sulfonate, phosphate esters, diphenyl ether sulfonates, and alkyl naphthalene sulfonates. On a cost-performance basis, DIACID 1550 would be the product of choice in most detergent applications.

We have shown that clear, aqueous nonionic surfactant solutions and pine oil disinfectant cleaners can be prepared with lower hydrotrope concentrations when a diacid soap is the hydrotrope. Also, high-solids soap solutions can be prepared by including diacid. When used in detergent formulations, diacid soaps help reduce the surface tension, reduce viscosity, and increase foaming, all of which should increase cleaning power when compared with formulations containing standard commercial hydrotropes. All of these advantages, along with the nontoxic and biodegradable nature, should make diacid surfactants attractive alternatives when considering the

TABLE 6

Ross-Miles Foam Heights for Diacid Potassium Soaps and SXS[a]

	1.0% Concentration		0.1% Concentration	
	Initial	5 Min	Initial	5 Min
D-1595	27	23	14	2
DIACID 1550	20	18	12	4
SXS	0	0	0	0

[a]Foam heights are given in cm.

TABLE 7

Hard-Water Compatibility Soap Scum Endpoint of 1% Soap Solution[a]

Sample	Soap	pH	300 ppm Volume (mL)	500 ppm Volume (mL)
D-1595	Sodium	10.5	0.72	0.49
	Potassium	10.5	0.58	0.46
	Ammonium	7.5	2.48	1.56
	TEA	7.5	2.35	1.27
DIACID 1550	Sodium	10.5	1.00	0.72
	Potassium	10.5	1.20	0.84
	Ammonium	7.5	3.10	2.01
	TEA	7.5	3.32	2.40
Coconut fatty acid	Sodium	10.5	0.86	0.58
	Potassium	10.5	0.95	0.66

[a]The greater the volume of hard water added prior to the soap scum endpoint, the greater the hard-water compatibility.

hydrotrope needs for modern soap and detergent formulations.

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