Industrial Utilization of C_{21} Dicarboxylic Acid

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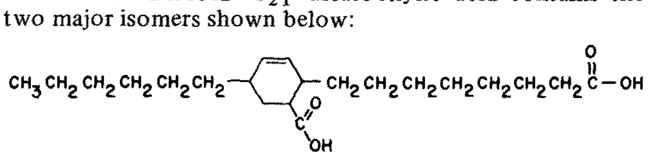
ABSTRACT

Interest in polyfunctional materials has increased steadily in recent years as polymer systems have become more prevalent in our society. One of the more unique and versatile of these products has only recently become commercially available, 5(6)-carboxy-4-hexyl-2-cyclohexene-1-octanoic acid. This C_{21} dicarboxylic acid not only has the expected ability to be incorporated into polymers for modification of the system, but it also has very unique surfactant properties. The sodium, potassium, and ammonium salts of this C_{21} dicarboxylic acid are unusually soluble in water, and the water solutions maintain relatively low viscosities even at high concentrations. The mono substituted derivatives of the C_{21} dicarboxylic acid are prepared easily, and they provide unique properties for a variety of end uses. This paper illustrates the potential industrial applications for the dibasic acid and some of its derivatives in ink resins; adhesives; coatings; lubricants; plasticizers; corrosion inhibitors; synthetic coolants; emulsions; temporary coatings; floor polishes; and industrial, household, and institutional cleaners.

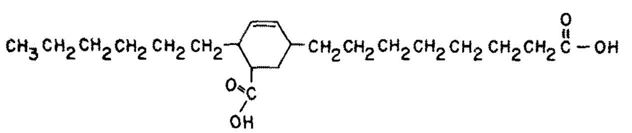
INTRODUCTION

For several years, it has been known that C_{21} dicarboxylic acid could be prepared by adding acrylic acid to conjugated linoleic acid in a Diels-Alder type reaction. However, the unique properties of this material were not appreciated until the recent commercialization of the product by the Custom Chemicals Department of Westvaco Corporation's Chemical Division. A desire for new polyfunctional materials has increased steadily as polymer systems have become more specialized. In response to this need, we have developed a commercial process for producing an extremely versatile difunctional material which has not only proved to offer useful property modification in polymer systems but also has very unusual surfactant properties and thus offers versatility to the formulator of industrial, household, and institutional cleaner and care products.

Westvaco DIACID C_{21} dicarboxylic acid contains the two major isomers shown below:



6 – CARBOXY – 4 – HEXYL – 2 – CYCLOHEXENE – 1 – OCTANOIC ACID



5 – CARBOXY – 4 – HEXYL – 2 – CYCLOHEXENE – 1 – OCTANOIC ACID

This C_{21} dicarboxylic acid is produced by reacting linoleic acid with acrylic acid in the presence of a catalyst. This is not a new reaction, and, in fact, a series of papers was published in the late 1950's by workers at the USDA Northern Regional Laboratory (1-3) covering this and similar products. However, the process (4) for preparing this product is unique and has made its commercial preparation feasible.

In spite of the interest in difunctional materials, there has not been a dibasic acid between 12-36 carbons commercially available until this C_{21} dibasic acid was introduced. It fills the gap between the available dibasic acids:adipic, azeleic, and sebacic at the lower end and C_{36} dimer at the high end. There was a C_{19} dibasic acid which the USDA laboratory at Peoria (5) investigated which was sampled by at least two companies, but it was never commercialized. The typical properties of the standard Westvaco grade of dibasic acid are shown in Table I. It contains better than 90% C_{21} dicarboxylic acid with the remainder being C_{18} monounsaturated fatty acid. As may be noted from the properties listed, it is a rather viscous liquid at room temperature, but the viscosity decreases rapidly on heating. The mol wt and the high polarity of the molecule result in a very low volatility for the dibasic acid and its derivatives. This cycloaliphatic dibasic acid is completely biodegradable as evaluated by means of the presumptive test of the Soap and Detergent Association (SDA), and it has an LD_{50} of 6.176 g/kg and is, thus, classified as nontoxic. It is soluble in many common solvents, such as alcohols, esters, ketones, ethers, chlorinated hydrocarbons, and aromatic hydrocarbons. Its solubility in aliphatic hydrocarbons is somewhat limited because of its very polar nature, and its water solubility is negligible. However, the salts are extremely soluble (6). This unusual solubility allows one to make high solids soaps for consumer and industrial uses. The salts are also excellent hydrotropes. They will solubilize nonionics in alkaline solutions or solubilize disinfectants in cleaner formulations.

Chemically, a dibasic acid of this structure will undergo three general types of chemical reactions. First of all, either

TABLE I

Typical Characteristics

Property	DIACID 1550
Acid number[a]	293
Saponification number	317
Dicarboxylic acid, %	92
Monocarboxylic acid, %	7
Unsaponifiables, %	1
Iodine number	62
Color, Gardner	6
Viscosity, 100 F, cSt	10,000
Viscosity, 210 F, cSt	160
Flash point, F	458
Fire point, F	507
Pour point, F	50
Refractive index @ 25 C	1.4855
Density @ 25 C	1.0241
Lb/gal	8.57
Vapor pressure, 400 F	0.2 MMHG
500 F	1.8 MMHG
LD_{50} – Acute oral, albino rats	6.176 g/kg

[a]The acid number is slightly lower than the saponification number because of the presence of some C-21 lactone. However, there is no loss of yield in the preparation of most derivatives, because the lactone converts normally to the salt, ester, etc., as does the acid.

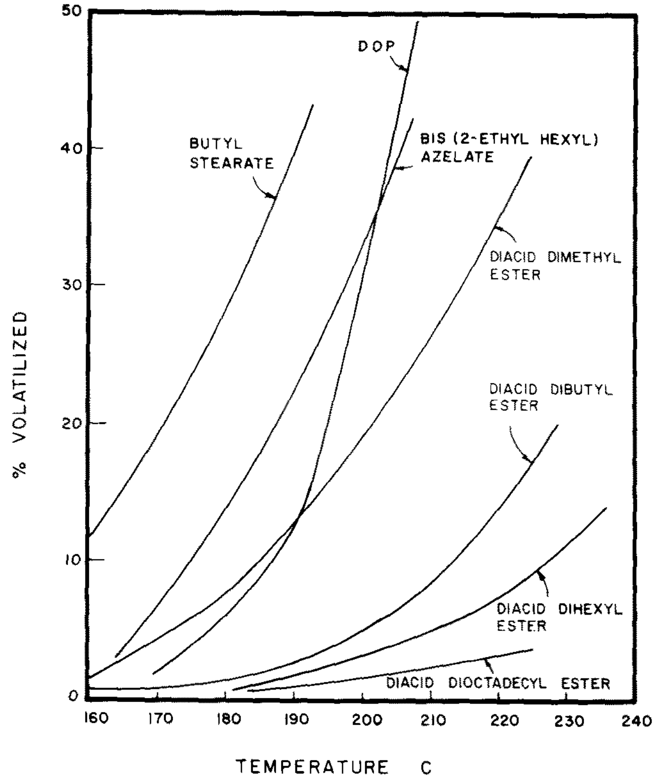


FIG. 1. Volatilization of esters with temperature; 2 hr at a given temperature. DOP = dioctylphthalate.

or both of the carboxyl groups can react. The carboxyl group is the primary reaction site and offers the unusual possibility for selectively carrying out a reaction on only one of the carboxyls. Secondly, a carbon-carbon double bond is present in the ring and is available for reaction. Third, reactions can occur on the α-positions relative to the carboxyl groups. We have keyed our work to the carboxyl group reactions. The carbon-carbon double bond seems to be about as active as the double bond in oleic acid. The carboxyl group will undergo a variety of reactions. As was stated earlier, the various salts are prepared easily and have unique properties. Also a variety of mono- and disubstituted acid derivatives can be prepared, as well as various polymeric structures. In polymeric systems, both the difunctionality and the double bond might be utilized. Many of the different derivatives have been synthesized and evaluated in various use applications. Rather than try to report all of this work, which is extensive, a few specific end use applications will be presented.

DISCUSSION OF END USES

One area that has been evaluated rather extensively is utilization of DIACID esters in lubricant formulations. This evaluation has not been limited to petroleum type lubricants but also has included textile lubricants and polyvinyl chloride (PVC) plasticizers. Several esters of the C_{21} dibasic acid have been prepared. The ester derivatives have low volatility, high smoke point, low viscosity, and generally are useful in areas where processing temperatures are relatively high. In Figure 1, volatility curves are shown for several materials used in the textile and PVC industries, as well as the curves for some of the esters of the C_{21} dicarboxylic acid. As will be noted, butyl stearate and bis-2-ethylhexyl azelate, which are used in the textile industry, and dioctylpthalate, which has been the work-horse of the plasticizer industry, are all more volatile than the DIACID esters. These properties demonstrate the potential advantages that might be realized if DIACID esters were utilized in the textile industry, in the PVC plasticizer area, and in automotive or jet engine lubricants.

DIACID esters have been evaluated as PVC additives due to their excellent low temperature properties and low volatility. Prior work at the USDA laboratories in Peoria (2) showed that these esters are compatible with PVC systems. Screening data for these esters illustrate the outstanding performance that can be expected in PVC plasticization (Table II).

DIACID salts can be used as stabilizers that are required to prevent the discoloration of PVC. The metal ion plays the

TABLE II

Typical Performance Characteristics of Plasticizers

Product	Concentration phr[a]	Tensile strength (psi)	Elongation %	Extraction rate, % Water[b]	1% Detergent[b]	Hexane[c]
DOP[d]	43	2250	160	0.2	0.5	22
C_{21} DIACID diamyl ester	42.8	1900	180	0.5	0.7	17
C_{21} DIACID dibutyl ester	47	1880	150	0.2	0.7	16

[a]For compound of standard modulus, 1500 psi at 100% elongation at 23 C.

[b]Extraction in 24 hr at 50 C.

[c]Extraction in 1 hr at 25 C.

[d]DOP = Dioctylphthalate.

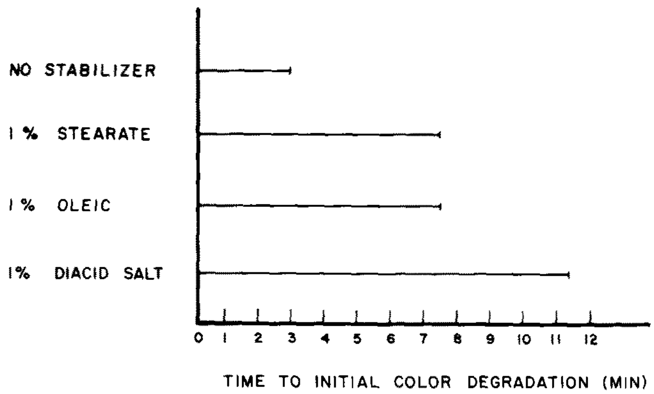


FIG. 2. Initial discoloration of polyvinyl chloride using zinc salts of various organic acids.

TABLE III

Corrosion Inhibition Data in 90/10 Iso-Octane-Water System at 30 C[a]

Additive	Rusting in hydrocarbon layer at various ppm additive				Rusting in aqueous layer at various ppm additive			
	50	25	10	7.5	50	25	10	7.5
None	P	P	P	P	P	P	P	P
Commercial inhibitor	E	E	G	G	E	E	E	G
C_{21} Dibasic acid	E	E	E	E	G	G	P	P
DIACID monoamide	E	E	E	E	E	E	E	G
DIACID ammonium 1/2 salt	E	E	E	G	E	E	G	P
DIACID amine salt	E	E	E	E	E	E	G	P

[a]Excellent (E) = no rust, good (G) = traces of rust, and poor (P) = rust.

major role in most stabilizers, but the organic carrier does have an effect. The organic carrier is especially useful if it can carry a higher percentage of metal into the PVC. Since this acid is bifunctional, it can carry almost twice as much metal/lb as can an oleic acid salt. Figure 2 summarizes the results of studies with various PVC stabilizers with one metal, zinc. These heavy metal salts also offer new opportunities as grease bases and dryers for coatings.

The C_{21} dicarboxylic acid is an extremely effective corrosion inhibitor. Several DIACID salts and amides, as well as the free acid, were compared with commercially available corrosion inhibitors in a static rusting test with cold rolled 1010 steel with excellent results (Table III). Potential utilization of DIACID derivatives is indicated for a variety of antirust applications, including: gasoline, fuel oils, oil well drilling, cooling towers, water recycle systems, etc. Various formulations would be desirable depending upon whether the systems were predominately water or hydrocarbon, but, generally, the dibasic structure offers a base for a variety of end use areas. In a more specific test for corrosion inhibition in a water system, the sodium, potassium, and diethanolamine salts of the C_{21} dicarboxylic acid proved to be very effective in preventing rust when substituted for sodium nitrite-triethanolamine in a synthetic coolant formulation.

Polyamides derived from the C_{21} dibasic acid have been prepared for evaluation in a number of applications. The reactive polyamides are excellent crosslinkers for epoxy resins, and the thermoplastic polyamides show promise for improving the properties of ink resins and adhesives. The final properties of the polyamide ink resins are virtually identical to those now commercially available, except for the gellation tendencies, where the material based upon the C_{21} acid is far superior to those based upon a C_{36} dibasic acid.

The diglycidyl ester of the C_{21} dicarboxylic acid is commercially available as EPI-REZ 5060 from Celanese Coatings Co., Louisville, Ky., and shows promise as a base for photocuring inks and as a modifier for epoxy resins, especially in electrical encapsulating applications.

As a crude approximation for surfactant behavior considerations, one can estimate the hydrophil-hydrophobe characteristics which might be expected by dividing the number of carbons in the molecule by the number of carboxyl groups present. Sebacic acid having a carbon to carboxyl ratio of 5 is too low to be in the surfactant range. Dimer acid, with a carbon to carboxyl ratio of 18, is on the higher end of the more common fatty acid surfactants and corresponds in some respects to stearic or oleic in surfactant properties. The C_{21} dibasic acid, with a ratio of carbon to carboxyl of 10.5, is at the lower end of the common fatty acid surfactants.

An evaluation of the actual hydrophil-hydrophobe character of the C_{21} material was obtained by adsorption tests from aqueous solution to various types of organic substrates. DIACID salts adsorb from aqueous solution to an aromatic substrate in the form of polystyrene latex to the same degree as a 13 carbon saturated monocarboxylic acid soap. On an aliphatic substrate in the form of polyethylene emulsion, DIACID salts adsorb from water to an extent comparable to the nine carbon saturated monocarboxylic acid soap, pelargonate. These values straddle the approximation proposed in the previous paragraph. The adsorption differences between substrates are primarily due to the

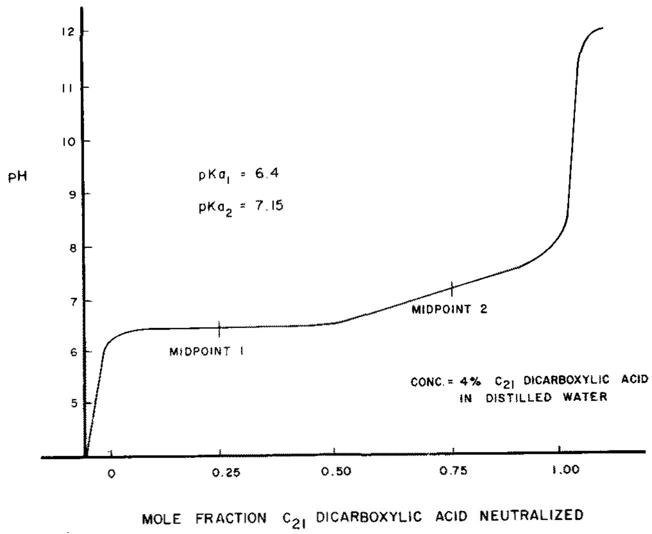


FIG. 3. Titration curve of C_{21} dibasic acid at 25 C with KOH.

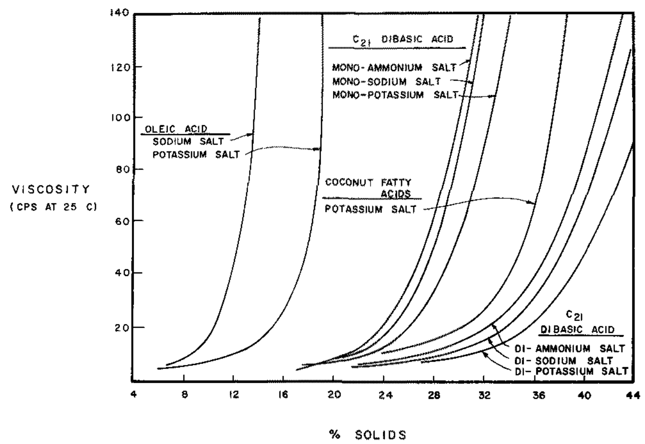


FIG. 4. Viscosity; concentration relationship of diacid salts. CPS = centipoise.

TABLE IV

Solubilizing of Nonionics in Alkaline Systems

DIACID-sodium salt 1:1 with nonionic[a]	Maximum concentration of NaOH	Maximum concentration of sodium silicate (2.50:1)[b]	Maximum concentration of KOH
Pluronic L-61	20.0%	23.0%	24.0%
Pluronic L-62	19.0%	18.5%	21.0%
Neodol 25-7	15%	20%	19%
Neodol 25-9	15%	18%	20%
Igepal CO-630	15%	<15%	19.3%
Plurafac RA-43	<10%	---	14%

[a]Mixtures are 57% solutions in water. The 1:1 ratio is on the basis of the anhydrous DIACID sodium salt.
[b]Percentages are silicate solids ($Na_2O + SiO_2$).

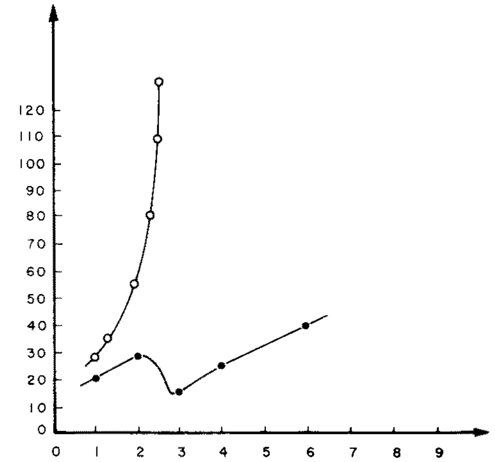


FIG. 5. Draves wetting time at 49 C. ○ = Igepal CO 630 0.10% and ● = 50% C_{21} diacid sodium salt and 50% igepal CO 630 (Total 0.10%).

affinity characteristics of the hydrophobe unit of the dibasic acid for the substrate. Previous work of this type has demonstrated the strong affinity of monounsaturated carboxylic acid soaps for aromatic substrates (7).

There is a difference between the reactivity of one of the carboxyl groups in the C_{21} dibasic acid and those in the dicarboxylic acids previously available. In the latter compounds, both of the functional groups are primary carboxyls, whereas in the C_{21} acid, there is both a primary carboxyl and a secondary carboxyl present. Such a situation permits greater selectivity and versatility in the derivatives which can be prepared than with the compounds having carboxyls of similar reactivity.

The simplest derivatives of importance as surfactants where this difference is demonstrated are the salts. In Figure 3, the titration curve for preparation of the DIACID dipotassium salt is presented. From this plot of pH vs mole fraction of C_{21} dibasic acid neutralized, it can be seen that the more acidic primary carboxyl group has a pKa of 6.4, whereas the secondary carboxyl group has a pKa of 7.15. Complete solubility of pure C_{21} dibasic acid occurs with neutralization of the primary carboxyl group. This low pH requirement permits the preparation of neutral salts. Such salts should be beneficial in applications where the comparatively alkaline fatty acid soaps are undesirable.

DIACID salts are unique in the degree of water solubility they possess. Figure 4 presents a comparison of the viscosity-concentration characteristics of both the mono- and di- ammonium, sodium, and potassium salts of the C_{21} dibasic acid with oleic and coconut soaps. It is seen that the DIACID salts remain low in viscosity at much higher solids than their monobasic acid counterparts. Even when the solids fall in the range of high viscosity, DIACID salts do not gel and become unworkable like monobasic fatty acid soaps. Thus, the DIACID potassium salt can be prepared as a water solution and easily handled up to 92% solids and the sodium salt up to 80% solids.

In addition to having excellent solubility by themselves, DIACID salts are capable of assisting greatly in solubilizing other substances into aqueous systems where these substances are normally quite insoluble. In addition, the dibasic salt often supplements the activity of the other substance so that less is required to achieve the desired results. Examples of this ability are shown in Table IV for

TABLE V

Formulation of Floor Polish

Ingredient	Rohm & Haas N-24-1	Rohm & Haas N-24-1
Latex		
Rhoplex B924 (38%)	31.6	31.6
Leveling resin		
SMA 17325 (15%)	5	---
Polyethylene emulsion		
Poly-EM 40 (15%)	15	---
Plasticizer		
Dowanol DE	4.0	---
Dibutyl phthalate	1.0	---
Tributoxyethyl phosphate (KP 140)	1.0	1.0
Wetting agent		
FC-128 (1%)	0.4	0.4
Experimental products		
DIACID ammonium soap (40%)	---	8.0
DIACID-oleic emulsified epolene E-10 polyethylene (15%)	---	15.0
Water	48.4	53.4

TABLE VI

Properties of Floor Polish

Criteria	Regular formulation	DIACID formulation
Streaking first application	Excellent	Excellent
Streaking second application	Excellent	Excellent
Streaking third application	Excellent	Excellent
Film clarity	Excellent	Good
Gloss	Poor	Excellent
Crazing	Good	Excellent
Cracking	Poor	Excellent
Water spotting	Excellent	Excellent
Detergent resistance	Stripped	Excellent
Formula appearance	Deep milky white	Slightly translucent

three highly alkaline materials in which nonionic surfactants are quite insoluble. Addition of an equal wt of the DIACID sodium salt to the nonionic produces soluble systems at the 15-20% alkali concentration common in alkaline cleaners. Solubilization of nonionics with the C_{21} dibasic acid improves the surfactant properties of alkaline systems considerably. Figure 5 demonstrates the improvements in Draves wetting time at various NaOH concentrations obtained when Igepal CO 630 is solubilized with the DIACID sodium salt. Here, better wetting results are achieved while using only half as much of the nonionic.

Another example of solubilizing with a DIACID salt is in the preparation of clear polyethylene emulsions for applications, such as floor polish. Clear anionic polyethylene emulsions can be prepared, using as the emulsifier, 25% less of a C_{21} dibasic acid-oleic acid blend than the currently popular distilled tall oil fatty acids. In addition, the C_{21} dicarboxylic acid is an effective plasticizer for polyethylene and other polymers. If the C_{21} dibasic acid is used in a floor polish formulation, the leveling resin and usually two of the three plasticizers can be eliminated (see Table V and VI).

In the homologous series of fatty acid soaps, those of intermediate chain length between lauric and stearic produce optimum foaming characteristics. DIACID salts by themselves are not especially impressive as foaming agents. However, Table VII demonstrates the dramatic foaming effect obtained by the addition of DIACID salt to a potassium oleate emulsified styrene-butadiene latex used in making foam rubber (8). These results show that both rate of foaming and volume of foam produced, as measured by foam density, are increased greatly over that obtained with equal amounts of oleic acid soap or dimer acid soap. Furthermore, much of this advantage is achieved with as little as 5% C_{21} dibasic acid based upon the total quantity of emulsifier.

TABLE VII

Effect of Added Soap upon Foaming Rate and Foam Density of Styrene-Butadiene Latex Emulsified with Potassium Oleate

Potassium soap	Time to top foam volume (sec)	Foam density (g/liter)
Oleic	85	131
C_{21} Dibasic acid	10	83
Dimer acid	90	165

The C_{21} dibasic acid is potentially quite useful in fabric softening. Its salts can be blended with long hydrocarbon chain cationic materials, used commercially for fabric softening, to produce a softener which can be added along with the detergent at the beginning of a wash. Table VIII shows detergency and softening comparisons between three different wt ratios of the dibasic acid to distearyl dimethyl ammonium chloride, a leading commercial wash cycle softener and a leading commercial rinse cycle softener. Within experimental variations, the best C_{21} acid based formula is equivalent in redeposition measurements and better in detergency than the commercial products. The DIACID compounds added in the wash cycle are better in softening power than the leading wash cycle softener but are not quite as good as the commercial rinse cycle product. A very effective rinse cycle softener can be based upon the C_{21} dibasic acid. Such a product can be formulated using the DIACID salts to replace ca. half of the quaternary amine.

The ability to carry out organic reactions selectively on the carboxyl groups of the C_{21} dicarboxylic acid is demonstrated in the preparation of alkanolamides. In Table IX, comparisons of lime soap dispersion and Draves wetting

TABLE VIII

Fabric Softener Results

			Redeposition (reflectance)[a]		Hand[a,b]	
Application	Product	Detergency ΔR	Durable press	Cotton	25% RH	65% RH
Wash cycle	Household wash cycle softener	8.8	81.6	85.1	3.0	2.0
Wash cycle	C_{21} Dibasic acid: distearyl dimethyl ammonium chloride by wt					
	1:1	10.4	81.4	85.7	2.6	2.0
	1:2	8.9	77.8	83.4	1.3	1.5
	1:3	7.8	80.7	85.6	2.3	1.5
Rinse cycle	Household rinse cycle softener	9.0	81.5	84.0	1.0	1.0

[a]Average of three runs for all tests, except detergency.

[b]Hand is in arbitrary softness units rated from 1 being the softest to 4 for wash to which no softener was added.

TABLE IX

Lime Soap Dispersion Index and Draves Wetting Times for 1:1 Monoethanol Amine Amides

Acid reactant	Lime soap dispersion index (%)	Draves wetting time (sec) 0.25% @ 50 C
Lauric-myristic	Insoluble	4
C_{21} Dibasic acid	5	14
DIACID monosodium salt	15	7

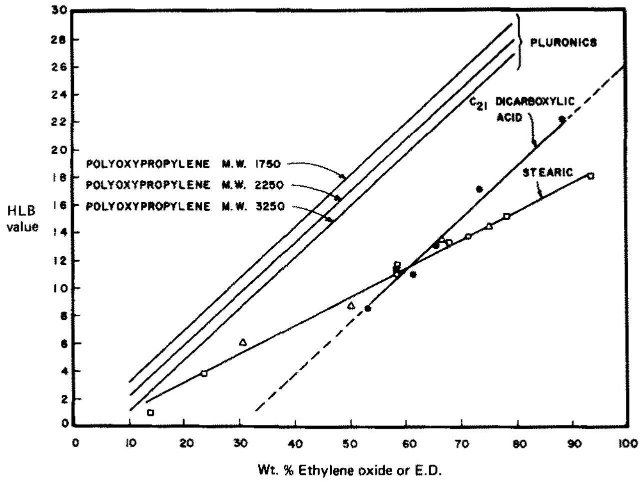


FIG. 6. Hydrophilic-lipophilic balance (HLB) vs wt percent ethylene oxide. EO = ethylene oxide, ○ = stearic, ■ = lauric, □ = oleic, and △ = tall oil fatty acid.

time are made of DIACID monoethanolamine amides, the mono sodium salt of the C_{21} acid, and a lauric-myristic blend. DIACID monoethanolamine amides are especially good lime soap dispersants requiring only 5% as much of the amide as the oleate soap in which it is blended to maintain precipitate free systems in hard water. DIACID bis-alkanolamides also have greater water solubility than their lauric and lauric-myristic counterparts but do not show quite as fast wetting characteristics. Wetting times of the DIACID half soap alkanolamides more nearly approach the results with lauric-myristic alkanolamides.

Another important class of surfactants in which DIACID derivatives have been evaluated is the ethoxylate esters. These compounds have been synthesized over a series containing 4-119 moles ethylene oxide/DIACID molecule.

The most widely accepted method of characterizing this class of nonionic surfactant is the hydrophilic-lipophilic balance (HLB) technique. Figure 6 presents a hydrophilic-lipophilic comparison between DIACID ethoxylates, several ethoxylated fatty acids, and the commercial Pluronic series of ethoxylated propylene oxide. The slopes of the HLB value vs percent ethylene oxide curves indicate that DIACID ethoxylates increase in HLB value with ethylene oxide addition at a rate more like the Pluronics than the fatty acids. This is probably because ethylene oxide adds to each of the carboxyls leaving the hydrophobe unit in the center of the molecule like the propylene oxide hydrophobe in the Pluronics.

One of the most outstanding properties of DIACID ethoxylates is their lime soap dispersion ability. In laundry detergency tests, shown in Figure 7, a formulation

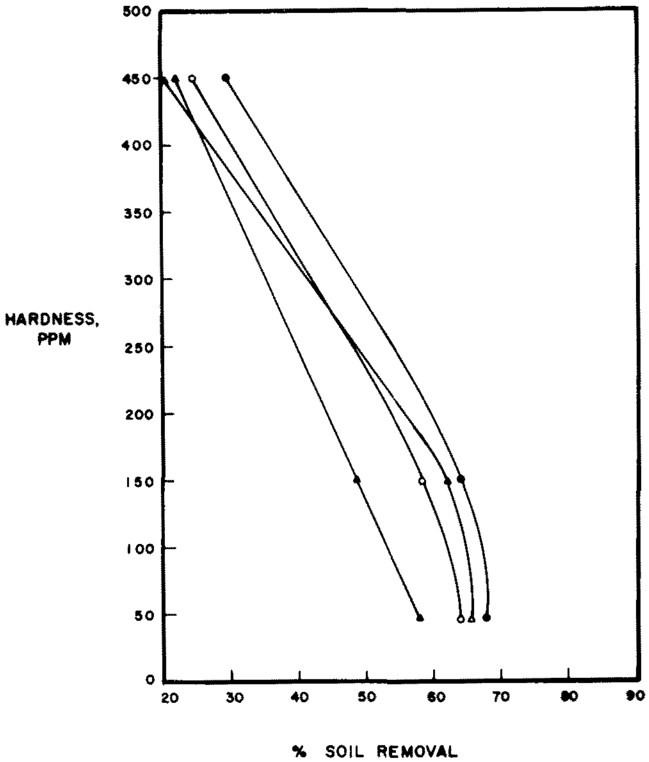


FIG. 7. Laundry detergency tests, lime-soap dispersion. ▲ = tallow soap, ● = diacid 22 mole ethoxylate, ○ = diacid 10 mole ethoxylate, △ = sodium tripolyphosphate built linear sodium alkylbenzene sulfonate pH 9.0, 100 F.

consisting of 65% tallow soap, 20% DIACID ethoxylate, (22 moles ethylene oxide) and 15% sodium metasilicate out-performs a standard polyphosphate built linear sodium alkylbenzene sulfonate (LAS) detergent over the entire range of $CaCO_3$ hardness. The more biodegradable 10 mole ethoxylate is better than the standard LAS formulation at high hardness concentrations but produces somewhat poorer cleaning than the LAS standard in the more normal hardness range.

These applications on which patents have been issued or are pending demonstrate the versatility that can be obtained by addition of hydrophylic functional groups to a fatty acid molecule. Evaluations of this type are being continued on a variety of multifunctional compounds.

This C_{21} dicarboxylic acid is a unique, newly available chemical which has unusual versatility. It offers improved performance in numerous end use applications.

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