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GUANIDINE SOAPS

Properties as Detergents

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Synthesis and properties of guanidine salts of fatty acids are described. These compounds demonstrate similarity to the usual alkali metal soaps. Detergent ability of the guanidine soaps is compared with the corresponding sodium and potassium compounds on such points as surface tension, emulsifying power, deflocculating power, and laundering. Possible uses for the guanidine soaps are suggested.

INVESTIGATIONS on the nature of guanidine, which have been proceeding at the Polytechnic Institute of Brooklyn under the guidance of G. B. L. Smith for many years, have uncovered many facts concerning its properties and possible applications (*10*). Its highly basic character led to the prediction that it should be capable of forming soap-type compounds with fatty acids, similar to those formed by the alkali metals.

PREPARATION OF GUANIDINE SOAPS

As starting materials, purest available c.p. grades of oleic and stearic acid, as well as a commercial coconut fatty acid, were procured. Guanidine carbonate was purified from solutions of the commercial salt in contact with activated charcoal, by reprecipitation with ethyl alcohol.

For the synthesis, the following procedure was found to be simple, practical, and capable of producing almost theoretical yields of the soaps.

Fatty acid was first dissolved in about ten times its weight of solvent (ethyl alcohol or acetone). A slight excess of pulverized guanidine carbonate was added, and the mixture was refluxed gently for about 2 hours. To test for completion of reaction, free uncombined alkalinity or acidity was determined by withdrawing a sample, filtering to remove excess guanidine carbonate, and titrating with standard acid or base as required. With 2 hours of refluxing, an equilibrium state was reached, after which no further reaction took place. The entire contents of the flask were then filtered, the major portion of the solvent was distilled off, and the residue was dried under vacuum.

Resultant soaps contained some moisture which was extremely difficult to remove without decomposition, but for the purposes of this study, they were considered to be sufficiently pure. Analyses by standard methods (*13*) yielded the results given in Table I.

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The appearance and properties of these soaps are not substantially different from the better known potassium and sodium soaps. Guanidine oleate is an amber pasty mass at room temperature, similar in appearance to potassium oleate. Guanidine stearate is a hard white substance possessing the soapy feel of ordinary cake soap. The soaps dissolve readily in water, yielding clear foaming solutions with good detergent properties. The solubility of the guanidine soaps in organic solvents is considerably greater than that of the corresponding alkali metal compounds. This property would automatically suggest their value as emulsifying agents in water and oil systems.

Since these compounds demonstrated the usual properties of soaps, it was decided to evaluate them as detergents. For comparison purposes, stock solutions of the sodium and potassium soaps of the three fatty acids used were prepared by reaction of stoichiometric quantities of fatty acid and alkali metal hydroxide in hot distilled water.

TABLE I. ANALYSIS OF GUANIDINE SOAPS

	%
Guanidine stearate	97.96
Free stearic acid	0.56
Moisture	0.92
Total (accounted for)	99.44
Guanidine oleate	92.68
Free oleic acid	0.97
Moisture	5.68
Total (accounted for)	99.33
Guanidine coconut soap	98.04
Free guanidine carbonate	0.04
Moisture	1.83
Total (accounted for)	99.91

TABLE II. SURFACE TENSION OF OLEATE SOAPS IN AQUEOUS SOLUTION AT 25° C.

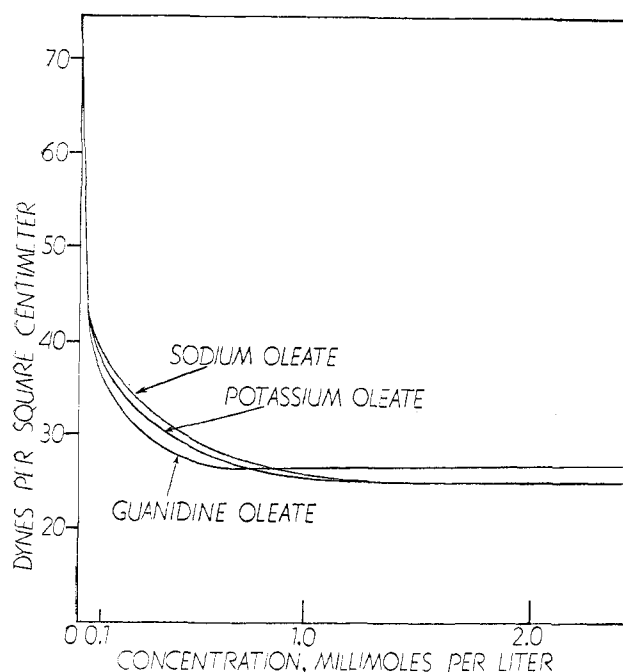| Concentration, % by Weight	Surface Tension, Dynes per Sq. Cm.		
	Guanidine oleate	Potassium oleate	Sodium oleate
0.50	27.4	25.4	25.4
0.20	27.1	24.7	25.1
0.10	27.0	25.0	25.1
0.05	26.9	25.1	25.2
0.02	27.6	27.7	27.0
0.01	30.9	31.6	31.4
0.005	35.8	36.6	36.1
0.002	39.2	37.7	39.6

Figure 1. Surface Tension of Oleate Soap Solutions

EVALUATION OF DETERGENT POWER

It is well established that no one simple physical or chemical test can truly indicate the ability of a solution to remove soil. Since no adequate yardstick exists by means of which a detergent value may be assigned to a compound, the authors have used the better known soaps for comparison purposes in a series of tests designed to exhibit relative detergent ability. Distilled water was used throughout these tests.

SURFACE TENSION PROPERTIES. Surface tension measurements were made at various dilutions using the Du Noüy tensiometer. To minimize errors due to evaporation, determinations were carried out within a waxed 1000-ml. Erlenmeyer flask according to a method described by Miles and Shedlovsky (4). Results

obtained for the oleate and coconut soaps are indicated in Tables II and III. Each reading represents an average of five determinations on two samples.

It is readily seen that guanidine soap solutions have surface tension properties that are comparable to those of the alkali metals. It would appear further that at low concentrations (below 0.02%) the guanidine soaps have superior surface tension lowering powers, whereas at higher concentrations the sodium and potassium soaps exhibit solutions of lower surface tension. This is graphically illustrated in Figure 1, where surface tension of the oleate soaps is plotted against molar concentration expressed as millimoles per liter.

ABILITY TO EMULSIFY OIL. This property of the detergent solutions was measured, comparatively, with the Donnan pipet (1, 2). By means of this apparatus, a measured volume of oil is released within the aqueous soap solution. The size and consequently the number of drops of oil formed will depend upon the interfacial tension existing between oil and solution. In this way, the relative emulsifying power of a detergent solution may be estimated by the number of drops released by a constant volume of oil. The superior emulsifying power of the guanidine soaps is well established by the high drop numbers obtained (Table IV).

DEFLOCCULATING POWER. The measurement of deflocculating or dispersing power is designed to reflect the ability of a solution to disperse soil, maintain it in suspension, and prevent its redeposition upon the cleaned surface. This property has been considered by many investigators one of the most telling indications of detergent power (9, 11, 12, 15).

Briefly, deflocculating power was measured by shaking a quantity of standard soil with a solution of the soap and measuring the amount of soil remaining in suspension after a predetermined settling period (6).

Deflocculating power of the various soaps expressed as grams of soil present in 100 ml. of solution is listed in Table V. The excellent ability of guanidine soaps to disperse soil is very evident from these values. Indeed, actual analysis was not required to note this characteristic, for after the 24-hour settling period, the cylinders showed striking differences in amounts of suspended matter. In all cases, the guanidine soaps produced deep brown opaque solutions, whereas in many cases the alkali metal soaps were almost transparent.

PRACTICAL WASHING TEST. The foregoing series of tests give a somewhat indirect indication of detergent power, but they may not necessarily reflect the ability of a substance to clean soiled fabric, as usually encountered. For this purpose, a practical washing test was run on woolen flannel which had previously been soiled under standardized conditions. The literature contains numerous references to this type of test, describing various soiling

TABLE III. SURFACE TENSION OF COCONUT SOAPS IN AQUEOUS SOLUTION AT 25° C.

Concentration, % by Weight	Surface Tension, Dynes per Sq. Cm.		
	Guanidine soap	Potassium soap	Sodium soap
1.00	26.2	27.2	26.3
0.50	26.3	23.9	24.4
0.20	25.4	23.9	23.5
0.10	24.9	23.7	22.9
0.05	24.4	25.1	25.2
0.02	26.8	28.4	28.6
0.01	32.9	33.5	33.6
0.004	38.3	39.4	38.8
0.002	49.4	48.2	49.5

TABLE IV. EMULSIFYING POWER AS DROP NUMBER AT 25° C.

(Drop No. of distilled water is 94)

Concentration of Soap Solution, % Oleate	Guanidine Soap	Sodium Soap	Potassium Soap
0.05	187	157	155
0.025	132	122	122
0.013	109	104	105
% Stearate			
0.05	103	106	106
0.025	100	101	103
0.013	98	99	99
% Coconutate			
0.05	138	127	127
0.025	108	106	104
0.013	96	96	95

TABLE V. DEFLOCCULATING POWER AT 25° C.

Determination	I		II		
Sample	1	2	1	2	Av.
Potassium oleate	0.018	0.018	0.021	0.020	0.019
Sodium oleate	0.020	0.019	0.019	0.019	0.019
Guanidine oleate	0.038	0.038	0.041	0.040	0.039
Potassium coconutate	0.004	0.004	0.006	0.005	0.005
Sodium coconutate	0.005	0.004	0.007	0.007	0.006
Guanidine coconutate	0.031	0.030	0.029	0.030	0.030

TABLE VI. PRACTICAL WASHING ABILITY

Soap	Per Cent Soil Removal			
	Test 1	Test 2	Test 3	Av.
Guanidine oleate	46.8	46.5	46.5	46
Potassium oleate	42.0	42.5	50.0	46
Sodium oleate	49.2	51.8	48.5	50
Guanidine stearate	48.0	46.7	48.4	48
Potassium stearate	46.7	48.2	50.0	48
Sodium stearate	50.0	54.0	52.1	52
Guanidine coconutate	72.3	77.4	68.8	73
Potassium coconutate	67.2	57.6	58.2	61
Sodium coconutate	71.9	78.7	80.7	77

mixtures, fabrics, and washing procedures (*3, 5, 7, 8, 14*). Washing was carried out in a Launder-O-Meter, using 0.25% soap solutions at a temperature of 45° C. Soil removal was calculated from reflectivity measurements of the fabric in its condition before and after soiling and after the cleaning operation. The values listed in Table VI point to the fact that guanidine soaps are about as good as the corresponding potassium soaps for laundry uses.

CONCLUSION

The typical soaplike properties of the guanidine soaps compare favorably with the usual alkali soaps. From a purely economic point of view, however, the future of these compounds probably does not rest with their value as cleaning compounds. They should find their major application as emulsifying agents. Possible uses may well be found in wax dispersions, drug and cosmetic preparations, food emulsions, and water emulsifying cutting oils. Other organic bases such as ethanolamines, morpholine, isopropylamines, and amino methyl propanol have been widely used for their ability to form fatty acid soaps possessing good emulsifying properties for water and oil. The guanidine soaps may conceivably have a future comparable with any of these.

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High-Solids Synthetic Latex Directly from Reactor

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Until recently high-solids synthetic latices were made only by expensive and time-consuming concentration of dilute latex. It is now possible to produce stable, fluid latices of 55–60% total solids content directly in the reactor. Average particle size approaches that of natural latex, and mechanical stability is excellent. Laboratory tests indicate that films from high-solids type III latex are equivalent to those from creams of normal type III.

Procedures and the required changes in equipment used in the polymerization of these latices are described. Since the changes are relatively simple, it is indicated that this development will relieve the consumer of most of the premium which at present must be paid for concentrated latices.

IN THE ten-year period preceding the outbreak of hostilities with Japan, imports of natural latex into the United States assumed a sharply rising trend. (Figure 1 shows that the 1940 figure is somewhat high owing to the inception of stockpiling.) Roughly 80% of this latex was shipped in as a concentrate of 60–65% solids, since this eliminated shipping excess water originally present in the latex, and constituted a material suitable for various applications in which the normal latex could not be used.

Although small quantities of special-purpose synthetic latices had been produced domestically prior to 1941, it was not until 1944 that substantial production of a general-purpose synthetic latex got under way (Figure 1). With this production, there arose the problem of producing a concentrate for use in applications where a high-solids latex is essential. Natural rubber latex can be concentrated readily, either by centrifuge or a creaming process, since it has a large particle size. Synthetic rubber latex, on the contrary, has a very small particle size, which

makes concentration a more difficult and costly operation. In practical creaming operations a significant amount of polymer is usually lost in the serum.

This article presents a description of two new synthetic latices made to 55–60% solids directly in the reactor and a short description of the methods of preparation. Since the production of these high-solids latices is only slightly more expensive than the production of low-solids types, they can be sold at only a small increase in cost over the latter.

PLANT EQUIPMENT CHANGES

In the production of high-solids latices several problems were encountered. The more troublesome were: (*a*) high viscosity and gelation of the latex, (*b*) high rate of heat evolution, (*c*) dying out of the reaction, and (*d*) difficulty in stripping due to foaming.

During the reaction the latex goes through a period of high viscosity which may cause gelation of the entire mass of latex in the reactor. This creates a serious heat-transfer problem in removal of the heat of polymerization. The problem is further complicated by the large proportion of monomers in the reactor batch, which necessitates the removal of a much larger total amount of heat than for type III latex taken to only 38% solids.

The plant reactor installation worked out to overcome the foregoing difficulties is shown in Figure 2. To circulate the viscous latex, the standard reactor agitators were replaced with duplex open-tilted Turbo impellers, in accordance with the recommendations of the Turbo-Mixer Corporation. This type of agitator was found to produce good circulation of the viscous material with moderate power consumption. The maximum power consumption thus far observed on a 3000-gallon reactor installation is 11 horsepower.

The method devised for removal of the excess heat of reaction