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Solid Nonionic Surface-Active Agents

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SINCE BENGEN'S DISCOVERY of urea adduct formation with linear aliphatic compounds (6) many investigators have substantiated and extended this work (10, 13, 14) and have sought practical applications of this phenomenon. The fractionation of fatty acids by urea adduct formation based on the chain length and on the degree of unsaturation of the fatty acids has been demonstrated (9, 11). The principles of adduct formation have also been applied to the pilot plant separation of hydrocarbons (1), and another field of practical application was opened with the discovery of urea-solidified nonionic surfactants (2, 3, 4). Some phases of this latter development are described here.

In the present work it is shown that the formation of the products is dependent on the configuration of the lipophilic portion of the molecule and on the length of the polyoxyethylene chain as well as the ratio of the urea to the surface-active agent. Some methods of preparation are described, and the surface-active properties of two commercially available detergents based on this discovery are demonstrated.

Experimental

Simple Mixing Process. The compositions shown in Table I were prepared by mixing the indicated proportions of the polyoxyethylene compound and urea (ground using a mortar and pestle) in a 150-ml. beaker. The mixture was stirred with a spatula for several minutes to give a homogeneous slurry, which was then allowed to stand at room temperature to harden.

Detergency Tests. 1,000 ml. of detergent solution of desired concentration were placed in one of the stainless steel beakers of the Baker Terg-O-Tometer,[1] and the solution was brought to temperature (140° F.). Four 4x4 in. ACH No. 114 soiled cotton swatches (7) were placed in the test solution after agitation had been started at 75 ± 3 cycles per minute (approximately 60 r.p.m.). The duration of the wash period was 10 min. and was followed by two 3-min. rinses in 1,000 ml. of water corresponding to the hardness of the wash water. The swatches were then removed from the solution, squeezed lightly by hand, and dried in an oven at 180-190°F. The reflectance of the soiled fabric was measured before and after washing with a Hunter Reflectometer, using the turntable method of mounting the fabric (12). The soil removal was then calculated by the following formula:

$$\%\ \text{Soil Removal} = R_w - R_s / R_u - R_s \times 100$$

where R_w = reflectance of the washed fabric
R_s = reflectance of the soiled fabric
R_u = reflectance of the unsoiled, unwashed fabric.

The results shown in Figures 1 and 2 were obtained by using two commercially available urea-solidified detergents (50% urea) and a commercial sodium dodecyl benzene sulfonate (85% active) on an "as is" basis.

Discussion

It was found that, by simple mixing, compositions containing certain surface-active agents of the polyoxyethylene type and urea will form fluids which become solid cakes on standing at room temperature. It was observed that heat is evolved in the mixing process and that expansion in volume occurs as the solidification proceeds. This process makes possible the preparation of solid nonionic surfactants with a wide range of properties and of high active ingredient content previously unobtainable. Examples of these solid compositions have been prepared and are recorded in Table I. The surfactants solidified in this manner are composed of a long chain lipophilic portion and a hydrophilic portion consisting of an oxyethylene chain

TABLE I

Solid Urea-Surface-Active Agent Compositions

Composition (%)		Surface-active agent	
Surface-active agent	Urea	Source of lipophilic portion of molecule	Average moles ethylene oxide[a]
10	90	Tall oil[b]	16
20	80	Tall oil[b]	16
30	70	Tall oil[b]	16
50	50	Tall oil[b]	16
50	50	Tall oil[b]	12
30	70	Tall oil[b]	8
30	70	Tall oil[b]	6
30	70	Rosin (abietic acid)	14
50	50	Rosin (abietic acid)	16
30	70	Lauric acid	8
30	70	Palmitic acid	20
30	70	Stearic acid	2
30	70	Stearic acid	15
30	70	Oleic acid	2
30	70	Oleic acid	8
30	70	Stearic acid (2 moles)[c]	35
30	70	Octadecyl amine	10
30	70	Oleic amide	16
30	70	Sorbitan monolaurate	10
30	70	Methanol	8
30	70	Methanol	12
30	70	Methanol	16
30	70	Lauryl alcohol	2
30	70	Lauryl alcohol	23
30	70	Octyl phenol	10
30	70	p-Tertiary amylphenol	9
50	50	Tridecyl alcohol	12
30	70	Polyethylene glycol[d]	....
30	70	Polyethylene glycol[e]	....

[a] Moles ethylene oxide/mole of surface-active agent.
[b] 46-50% fatty acids; 43-47% rosin acids; 7½% sterols, higher alcohols, etc.
[c] Polyoxyethylene (35) stearic acid stearate.
[d] Polyethylene glycol, average molecular weight 400.
[e] Polyethylene glycol, average molecular weight 1000.

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[1] Baker Instrument Company, now manufactured by the U. S. Testing Company.

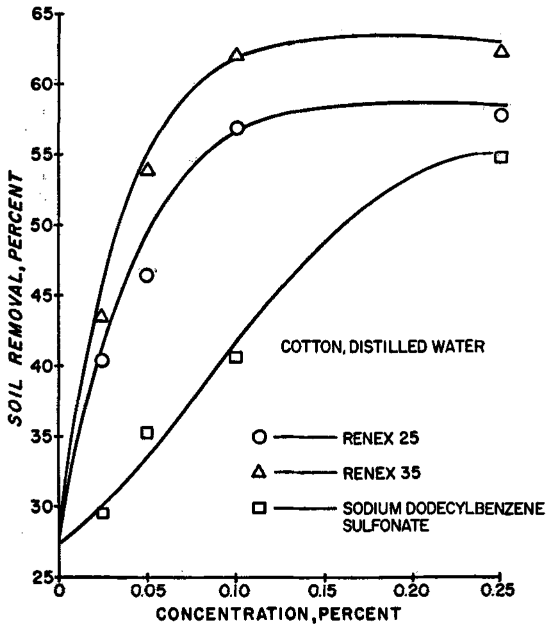

FIG. 1

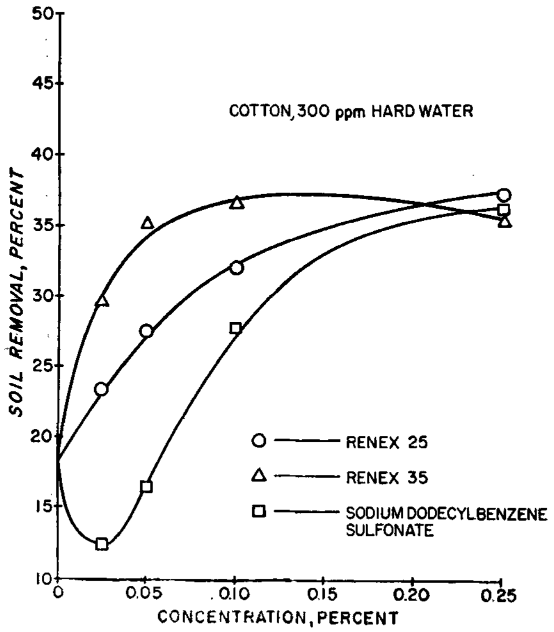

FIG. 2

of varying length. In many cases the lipophilic portion of the surface-active molecule contains at least some straight chain radicals. However in some cases the lipophilic portion consists of aromatic or branched chain aliphatic components which might not be expected to form urea adducts according to present theories. Examples of these non-straight chain molecules are polyoxyethylene rosin, polyoxyethylene p-tertiary amyl phenol, and a polyoxyethylene derivative of a highly branched tridecyl alcohol.

The published theories of urea complex formation are believed to apply to the urea adducts of the polyoxyethylene type of nonionic surface-active agents (8). Briefly the theory maintains that the crystal has a hexagonal unit cell composed of molecules of urea arranged in spirals. In the adduct the urea molecules are held together by spirals of hydrogen bonds between the oxygen atoms and the amide groups. The complexing molecule is pictured as fitting into the hollow axis of this spiral.

In the case of surfactants of the polyethylene glycol derivative type it is believed that the hydrophilic group takes part in the adduct formation since any compound with a sufficiently long polyoxyethylene group will solidify with urea. This does not preclude the possibility of the lipophilic group also entering into adduct formation. In some compounds both the polyoxyethylene chain and the lipophilic portion of the molecule may be involved in adduct formation. For example, a polyethylene glycol solidifies with urea, as does a polyoxyethylene highly branched tridecyl alcohol. On the contrary, the highly branched tridecyl alcohol will not form adducts with urea. Oleic acid forms adducts with urea as does the polyoxyethylene oleic acid. It has also been found that polyoxyethylene lauryl alcohol containing as low as two (average) oxyethylene groups per mole will form a hard product with urea whereas a similar derivative of the highly branched tridecyl alcohol will not solidify.

Applications of the Process

These urea adducts of the nonionic surface-active agents can be prepared in the form of powders, flakes, pellets, tablets, or bars. The powders and flakes possess the advantages of all free-flowing solids including ease of blending with alkalies and other dry materials. The surface-active properties of the products can be varied to give predominantly detergent, wetting, or emulsifying characteristics by selection of the surfactant.

If the process of simple mixing is used, the rate of hardening is accelerated by the use of urea of very small particle size. Another means of increasing the rate of hardening is to use a dough mixer which gives a considerable amount of shearing force during the mixing operation. If the mixing is to be followed by milling, the extent of preliminary mixing, with many compounds, must be controlled to prevent too rapid hardening. Other ingredients, such as perfumes, dyes, gums, alkaline builders, insecticides, germicides, and solvents, may be added during the mixing or milling operation. If desired, the urea-surfactant mixture may be cast in molds instead of milling into flakes and then pressing into tablets or bars. The powdered products are best prepared by cooling a finely divided liquid formed by forcing a molten mixture of urea and surfactant through a fine nozzle.

Two commercially available solid nonionic detergents are based on this process. One is Renex 25,[2] a complex composed of 50% urea and 50% polyoxyethylene tall oil. The other is Renex 35,[3] a white powder which is a complex composed of 50% urea and 50% polyoxyethylene tridecyl alcohol.

These products show the excellent soil removal properties of nonionic detergents. The cotton detergency of these compositions has been evaluated in the laboratory with the results shown in Figures 1 and 2, using a sodium alkylaryl sulfonate for comparison. The detergency of these solid nonionics is superior to that of sodium alkylaryl sulfonates at low concentrations. They both respond well to alkaline builders,

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[2] Registered Trade Mark, Atlas Powder Company, Wilmington, Del.

[3] Registered Trade Mark, Atlas Powder Company, Wilmington, Del.

TABLE II

Detergent Compositions
Composition (Percentage)

	Renex 25[a]	Renex 35[b]	Sodium Dodecyl Benzene Sulfonate[c]	Sodium Sulfate[d]	CMC[e]	Sodium Metasilicate[f]	TSPP[g]	STPP[h]
A.	20.0	......	......	3.5	2.0	10.0	30.0	34.5
B.	......	20.0	......	3.5	2.0	10.0	30.0	34.5
C.	......	......	23.5	....	2.0	10.0	30.0	34.5
D.	10.0	......	11.8	1.7	2.0	10.0	30.0	34.5
E.	......	10.0	11.8	1.7	2.0	10.0	30.0	34.5

[a] 50% polyoxyethylene tall oil.
[b] 50% polyoxyethylene tridecyl alcohol.
[c] 85% sodium dodecylbenzene sulfonate.
[d] Anhydrous.
[e] Sodium carboxymethyl cellulose—Hercules, low viscosity, type 70.
[f] Metso granular.
[g] Tetrasodium pyrophosphate.
[h] Sodium tripolyphosphate, anhydrous.

with which they are easily blended. Again, the detergency of these built compositions is superior to similarly built sodium alkylaryl sulfonates as shown in Figure 3. The exact compositions are given in Table II. The addition of these solid nonionics to built sodium alkylaryl sulfonates enhances their hard water detergency as previously reported for nonionic detergents (5). This effect on the detergency of alkylaryl sulfonates in built compositions is shown in Figure 4.

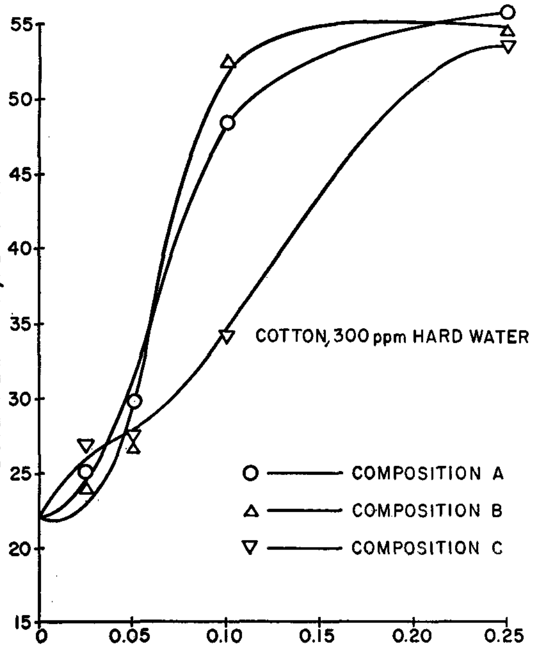

FIG. 3

Perhaps it should be noted here that the urea in these compositions has no significant effect on the detergency of these nonionics under the conditions of this test, using artificially soiled cotton.

TABLE III

Surface and Interfacial Tensions—Solid Nonionic Surfactants

Concentration (%)	Surface tension dynes/cm., 25°C.		Interfacial tension vs. Nujol, dynes/cm., 25°C.	
	Renex 25	Renex 35	Renex 25	Renex 35
0.001	58	46	24	22
0.01	39	33	10	12
0.10	39	30	6.2	5.0
1.0	37	30	5.3	4.5
5.0	37	29	4.3	3.3

The surface tensions and interfacial tensions of aqueous solutions of these products are recorded in Table III.

The foaming characteristics of these products, as measured by the Ross-Miles foam test, are recorded in Table IV. Renex 25 is a low foaming product, and Renex 35 is a relatively high foaming detergent.

TABLE IV

Ross-Miles Foam Test

25°C.

Compound	Concentration (%)	Foam height (mm.)	
		Initial	After 5 minutes
Renex 25	0.25	21	19
Renex 25	0.50	24	20
Renex 25	1.0	35	31
Renex 35	0.25	95	80
Renex 35	0.50	215	180
Renex 35	1.0	275	233

The wetting properties of these products as measured by the Clarkson-Draves test are given in Table V.

Summary

Methods have been described for converting liquid nonionic surface-active agents of the polyoxyethylene

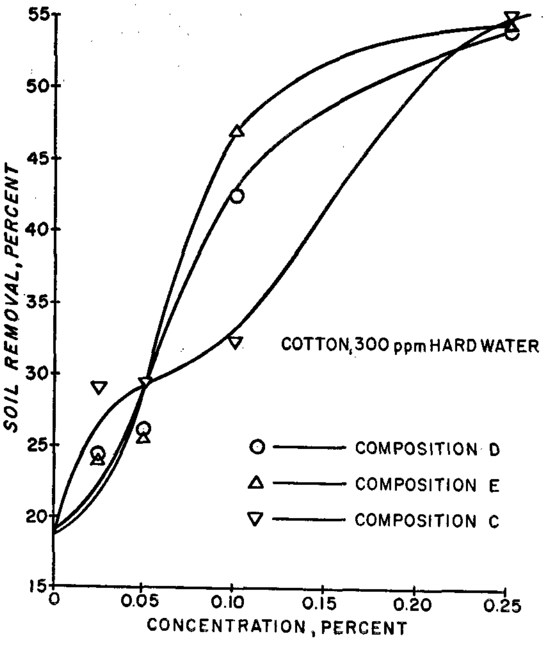

FIG. 4

TABLE V
Draves' Wetting Times

Concentration (%)	0.01	0.05	0.10	0.25	0.50	1.0
	Second, 25°C.					
Renex 25	......	......	>300	250	160	148
Renex 35	>300	170	31	8.0	3.5	instantaneous

type to solid compositions by complexing with urea. It is shown how these solid products may be made in the form of free-flowing powders, flakes, bars, pellets, or tablets.

The surface-active properties of two commercial detergents based on this discovery are reported. Besides showing the excellent detergency of these products in washing artificially soiled cotton, it has been shown that they enhance the detergency of alkali-built sodium alkylaryl sulfonates in hard water.

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Catalysis of Linoleate Oxidation by Copper-Proteins

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COPPER is a well known catalyst for the oxidation of unsaturated fats. Copper also catalyzes the oxidation of ascorbic acid and various polyphenols. Copper-protein enzymes occur in nature which specifically catalyze the oxidation of ascorbic acid and polyphenols (1). Also model ascorbic acid oxidases and polyphenolases can be made by adsorbing ionic copper on proteins. This analogy has been extended to show that copper-protein complexes give greater catalysis of unsaturated fatty acid oxidation than does copper alone.

Catalysis of unsaturated fat oxidation by copper-proteins may be the cause of oxidative fat rancidity in butter and other dairy products. A copper-protein occurs naturally in milk (2), and most of the copper found in butter has been isolated in the form of copper-protein complexes (13).

The iron porphyrin compounds, hemoglobin and myoglobin, are powerful oxidation catalysts for unsaturated fats (12). The results of this research indicate that hemocyanin, the oxygen transporting copper-protein of some invertebrates, is similarly a catalyst for unsaturated fat oxidation.

Experimental

Highly purified linoleic acid (Hormel Foundation) was neutralized with ammonium hydroxide to form a homogeneous 0.1 M ammonium linoleate solution and was stored under pure nitrogen at —20°C. Dilution of 0.1 M ammonium linoleate with 0.1 M sodium phosphate buffer at pH 7.0 produced a stable colloidal suspension of linoleate which was used in this study.

The proteins used in this study included purified conalbumin, crystalline bovine serum albumin (Armour and Company), and sodium caseinate (Nutritional Biochemicals Company).

Oxygen absorption measurements at 0° C. were made by conventional techniques, using a refrigerated Warburg respirometer. The main compartment of the reaction flask contained 3 ml. of colloidal linoleate dispersed in 0.1 M phosphate buffer pH 7.0 and at a concentration which resulted in 0.02 M linoleate in the final reaction mixture. One-half ml. of protein to give a final concentration of 1×10^{-4} M was mixed with 0.5 ml. copper sulfate in the side

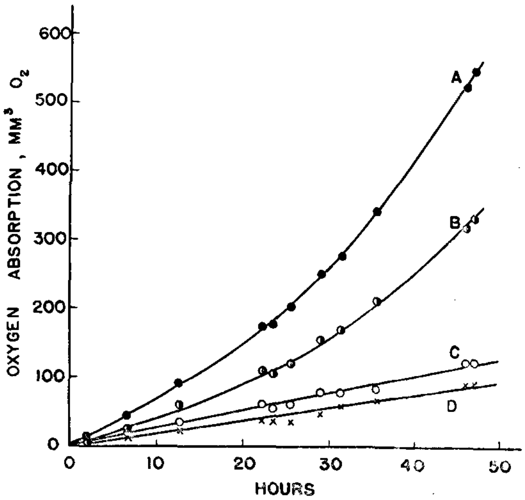

FIG. 1. Catalysis of linoleate oxidation by ionic copper and copper-proteins.

A. 1×10^{-3} M copper $+ 1 \times 10^{-4}$ M conalbumin
B. 1×10^{-4} M copper $+ 1 \times 10^{-4}$ M conalbumin
C. 1×10^{-3} M copper
D. 1×10^{-4} M copper