residual solvent. This represents higher boiling material from the petroleum solvent used, which has a boiling range of 150°–200°C.

The odor associated with the residual solvent can be removed by steam stripping in a conventional stripping column to a residual solvent content of 0.1% or less.

Sulfur Content

Tests in accordance with A.S.T.M. method D117-43 have always shown that solvent grease is sulfur-free. Some discoloration of the copper strip usually occurs, but sulfur cannot be detected in the discolored film.

REFERENCES

1. Sinclair, F.J., Proceedings Internat. Wool Text. Res. Conf., 1955, C.S.I.R.O., Melbourne, p.E-347.
2. Report No. G10, C.S.I.R.O., Division of Textile Industry, Geelong, Australia (1960).
3. Freney, M.R., C.S.I.R. (Australia), Bulletin No. 130, 1940.
4. Gillam, N.W., J. Aust. Chem. Inst., *14*, 361 (1947).
5. Horn, D.H.S., J. Sci. Food Agric., *9*, 632 (1958).
6. Truter, E.V., "Wool Wax," Cleaver-Hume Press Ltd., London, 1956, p. 229.

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Analysis of Mixtures of Ionic and Nonionic Surface-Active Agents. Separation and Recovery of Components by Batch Ion Exchange[1]

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Mixtures of anionic and nonionic surfactants or cationic and nonionic surfactants can be separated by stirring an aqueous solution of the mixture with a small amount of a strong anion exchange or strong cation exchange resin, respectively. The resin-ionic surfactant complex is removed by filtration and washed; the nonionics are recovered from the filtrate and washings.

By suitable treatment the ionic surfactants can be removed selectively from the resin. In the case of anionic surfactants, soaps, alkyl sulfates, and alkylaryl sulfonates can successively be removed from the resin; with cationics, nonquaternary and quaternary surfactants can be selectively removed. Results obtained with various mixtures of surface-active agents are discussed.

A NUMBER of years ago the separation of nonionic surface-active agents from mixtures with anionics by ion exchange resins, using a batch technique rather than the usual column method, was described (1). In this batch method an aqueous solution or dispersion of the surfactant mixture was stirred with a relatively small amount of an anion exchange resin, which complexed the anionic surfactants without removing any of the nonionic material. After the anion exchange resin with its complexed anionic surfactant had been removed by filtration and washed well with alcohol, the nonionic was recovered from the filtrate and washings. Results obtained with 14 binary mixtures of nonionics and anionics, representing all the major types available commercially, showed that the nonionic could be recovered in substantially quantitative yield by this method.

In the present paper the method has been extended to the separation of nonionics from their mixtures with cationics and, even more significantly, to the separation and recovery of the anionics and cationics complexed with the ion exchange resin.

Experimental

Separation of Nonionics from Their Mixtures with Cationics. Four to five grams of the surfactant mixture, dissolved or dispersed in 100 ml. of distilled water, are stirred for 4–5 hrs. with 20 g. of purified, 200–400 mesh, Dowex 50-X4 acid form cation exchange resin,[2] maintaining the mixture acid to Congo red during the stirring period by the addition of dilute hydrochloric acid, if necessary. (The Dowex 50-X4 resin is purified by stirring it for 15 min. with methanol, at least twice, until a colorless filtrate is obtained.)

TABLE I

Separation and Recovery of Nonionics from Mixtures with Cationics

No.	Mixture (wt.)[a]	Nonionic Product			
		Yield	n_D^{25}		Cationic test[b]
			Obsd.	Theor.	
1.	Pluronic L62 (1.04 g.) Ethomene C/25 (1.32 g.) Arquad 2HT (1.28 g.)	98% (1.02 g.)	1.4534	1.4540	—
2.	Brij 30 (1.61 g.) Amine 220 (1.53 g.) Cationic SP (1.77 g.)	99% (1.59 g.)	1.4531	1.4520	—
3.	Igepal CO-710 (2.20 g.) Armeen SD (2.19 g.) BTC (2.02 g.)	103% (2.27 g.)	1.4847	1.4842	—

[a] 100% actives basis.
[b] Kortlandt, C., and Dammers, H.F., J. Am. Oil Chemists' Soc., *32*, 58 (1955).

After the surfactant mixture is stirred with the resin for 4–5 hrs., it is filtered, and the resin is washed well with 95% ethanol. The nonionic material in the filtrate and washings is obtained by neutralizing the filtrate and washings to phenolphthalein with dilute sodium hydroxide, evaporating them to dryness, and extracting the residue with acetone to separate it from the inorganic salts. After removal of the acetone on the steam bath, the residue is dried briefly in the oven at 110°C. and is weighed.

Results obtained by use of this method are given in Table I. The results are comparable to those obtained previously for the separation of nonionics from their mixtures with anionics, using anion exchange resins in a batch procedure (1). The nonionic is recovered in substantially quantitative yield and is of good purity, as evidenced by the negative results

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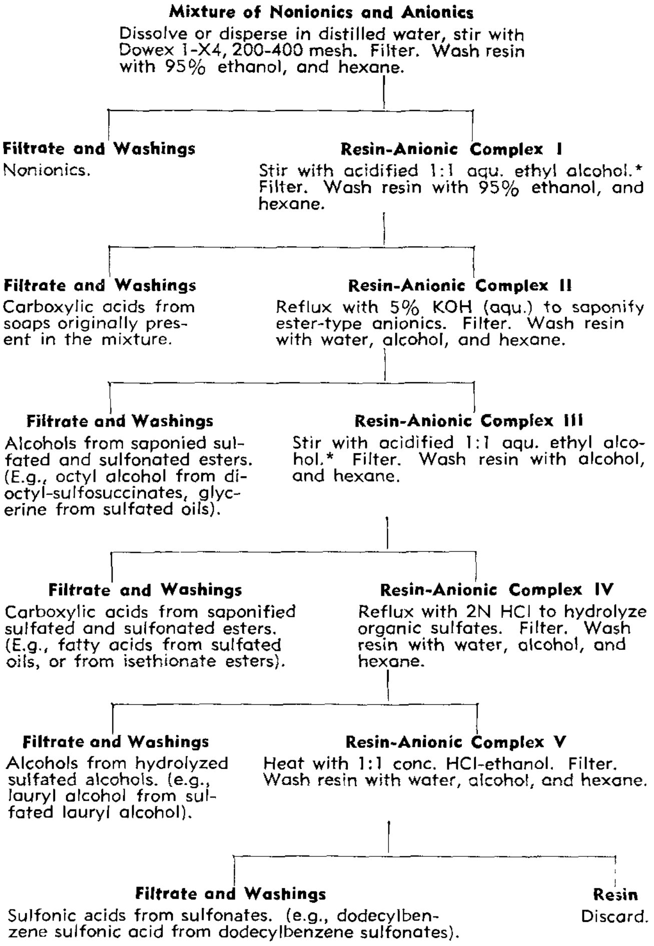
[1] Presented at the 51st fall meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

[2] Dow Chemical Company, Midland, Mich.



Mixture of Nonionics and Anionics
Dissolve or disperse in distilled water, stir with Dowex 1-X4, 200-400 mesh. Filter. Wash resin with 95% ethanol, and hexane.

Filtrate and Washings
Nonionics.

Resin-Anionic Complex I
Stir with acidified 1:1 aqu. ethyl alcohol.* Filter. Wash resin with 95% ethanol, and hexane.

Filtrate and Washings
Carboxylic acids from soaps originally present in the mixture.

Resin-Anionic Complex II
Reflux with 5% KOH (aqu.) to saponify ester-type anionics. Filter. Wash resin with water, alcohol, and hexane.

Filtrate and Washings
Alcohols from saponied sulfated and sulfonated esters. (E.g., octyl alcohol from dioctyl-sulfosuccinates, glycerine from sulfated oils).

Resin-Anionic Complex III
Stir with acidified 1:1 aqu. ethyl alcohol.* Filter. Wash resin with alcohol, and hexane.

Filtrate and Washings
Carboxylic acids from saponified sulfated and sulfonated esters. (E.g., fatty acids from sulfated oils, or from isethionate esters).

Resin-Anionic Complex IV
Reflux with 2N HCl to hydrolyze organic sulfates. Filter. Wash resin with water, alcohol, and hexane.

Filtrate and Washings
Alcohols from hydrolyzed sulfated alcohols. (e.g., lauryl alcohol from sulfated lauryl alcohol).

Resin-Anionic Complex V
Heat with 1:1 conc. HCl-ethanol. Filter. Wash resin with water, alcohol, and hexane.

Filtrate and Washings
Sulfonic acids from sulfonates. (e.g., dodecylbenzene sulfonic acid from dodecylbenzene sulfonates).

Resin
Discard.

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* Maintain mixture acid to Congo red with dilute hydrochloric acid.

Fig. 1. Separation and recovery of components of mixtures of nonionics and anionics.

in the qualitative test for cationics and the good correspondence between expected and observed refractive indices of the recovered nonionics.

Separation and Recovery of Mixtures of Nonionics and Anionics. Investigation of the complex formed between various anionic surfactants and the anion exchange resin, Dowex 1-X4, showed that the complex formed between this type of resin and the sulfonate or sulfate groups of anionic surfactants is very stable and is unaffected by changes in pH whereas the complex formed with the carboxylate type of anionic, such as soap, is decomposed at low pH. This permits the selective removal of the carboxylate type of anionic from the resin without affecting the complexed sulfates or sulfonates. Moreover the complex between this type of resin and the sulfonate or sulfate group is so stable that it is unaffected when heated in the presence of dilute, aqueous alkali or acid. This permits the selective removal of the components of saponifiable ester types of anionics or hydrolyzable sulfate types of anionics without interference from sulfonate- or sulfate-containing fragments.

Based upon these considerations, the scheme outlined in Figure 1 for separating mixtures of nonionics and anionics and recovery of their components was developed. Results obtained by use of this method are given in Table II. The recovery of anionic components is not quantitative; the usual yield approximates 80% of the theoretical value. However the quality of the component recovered is satisfactory for identification purposes, as evidenced by the good agreement between observed and theoretical values for refractive index and equivalent weight. Nonionics are recovered in substantially quantitative yield.

TABLE II

Recovery of Nonionics and Anionic Components from Mixtures

No.	Mixture (wt.)[a]	Recovery of Components		
		Yield	n_D^{25}	
			Obsd.	Theor.
1.	Igepal CA-710 (1.00 g.)	103% (1.03 g.)	1.4894	1.4890
	Na Oleate (1.90 g.)	82% (1.50 g. oleic acid)	1.4618	1.4640
2.	Brij 30 (1.00 g.)	98% (0.98 g.)	1.4530	1.4520
	Aerosol OT (1.00 g.)	85% (0.50 g. 2-ethylhexanol)	1.4285	1.4300
	Duponol WA (0.73 g.)	68+% (0.23+g. lauryl alcohol)[b]	....	....
3.	Span 20 (1.50 g.)	97% (1.45 g.)	1.4748	1.4740
	Tergitol 7 (1.20 g.)	94% (0.83 g. C_{17} alcohol)	1.4530	....
	Hyponate L (1.33 g.)	84% (1.11 g. free sulfonic acid)	419[c]	415-430
4.	Igepal CA-710 (1.00 g.)	101% (1.01 g.)	1.4910	1.4890
	Santomerse 3 (2.50 g.)	72% (1.70 g. free sulfonic acid)	324[c]	326

[a] 100% actives basis.
[b] Some lost because of volatilization.
[c] Eq. wt.

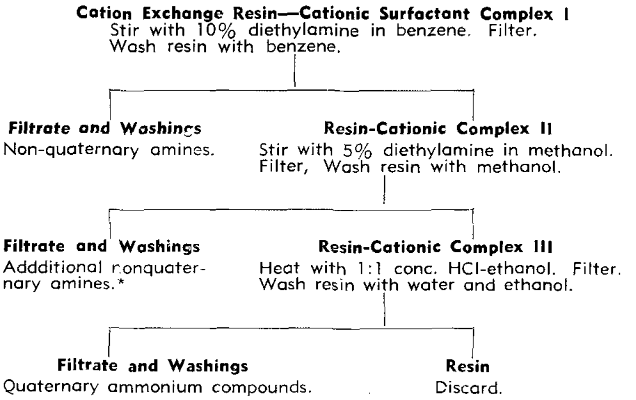
Separation and Recovery of Quaternary and Nonquaternary Cationics Complexed with Cation Exchange Resin. Investigation of the complex formed between various cationics and the cation exchange resin, Dowex 50-X4, showed that in an alkaline medium, the complex formed between this type of resin and quaternary ammonium salts is more stable than that formed with nonquaternary ammonium salts. By raising the pH, it therefore appeared possible to remove the nonquaternary cationics from the resin, leaving behind the quaternaries. In practice however this proved more difficult to accomplish than expected. Conditions which gave good recovery of the nonquaternary cationic yielded a product which was contaminated with quaternary cationic while conditions which yielded a nonquaternary cationic uncontaminated with quaternary cationic gave poor recovery of the former. Conditions were finally found which gave uncontaminated products in fair yield. These involved stirring the resin-cationic complex with a benzene solution of diethylamine, which is basic enough to displace nonquaternary cationics from

TABLE III

Recovery of Cationics from Mixtures

No.	Mixture (wt.)[a]	Recovery of Components			
		Yield (%)	Properties		
				Obsd.	Theor.
1.	Armeen SD (2.19 g.)	76 (+19)[1]	n_D^{25}	1.4601	1.4584
	BTC (2.02 g.)	81			
2.	Alkaterge C (1.46 g.)	91 (+12)[1]	—4° Amine test[2]		
	Hyamine 1622 (2.04 g.)	93	—Alkylolamine test[3]		
3.	Amine 220 (2.10 g.)	85 (+8)[1]	n_D^{25}	1.4903	1.4910
	Hyamine 1622 (2.02 g.)	92			
4.	Armeen SD (2.13 g.)	94 (+6)[1]	n_D^{25}	1.4607	1.4584
	Hyamine 1622 (2.13 g.)	91			

[1] Additional yield, contaminated somewhat.
[2] Van der Hoeve, J.A., J. Soc. Dyers and Colourists, *70*, 145 (1954).
[3] Rosen, M.J., and Goldsmith, H.A., "Systematic Analysis of Surface-Active Agents," Interscience Publishers, New York, 1960, pp.118–119.
[a] 100% actives basis.



* Small amount, somewhat contaminated with quaternaries. For estimation purposes only.

FIG. 2. Separation and recovery of quaternary and nonquaternary cationics complexed with cation exchange resin.

their complex with the resin but does not remove quaternary ammonium compounds. The scheme of separation is given in Figure 2. The Cation Exchange Resin—Cationic Surfactant Complex used in Figure 2 is that obtained from the procedure for the separation of nonionics from their mixtures with cationics, above.

Results obtained by use of the procedure in Figure 2 are given in Table III. If yields of contaminated nonquaternary cationics are included for estimation purposes, the recovery of this type of cationic is substantially quantitative. Slight losses are encountered in the recovery of the quaternary cationics because of the removal of some along with the nonquaternary cationics.

REFERENCE

1. Rosen, M.J., Anal. Chem., *29*, 1675–1676 (1957).

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Characterization of Oils from Low-Gland and Glandless Cottonseed[1]

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New varieties of cotton which contain few or no gossypol pigment glands are being developed. Commercial production of such varieties should contribute to improving meal quality and reducing the color problems encountered with cottonseed oil. Samples of gland-containing, low-gland, and glandless seed grown in California were obtained, and the oils were extracted and characterized.

With regard to the over-all characteristics the oils from the low-gland and glandless seed were indistinguishable from regular cottonseed oil. Iodine values, contents of unsaponifiables, cloud- and pour-points, response to the Halphen test, and similar characteristics resembled those of commercial cottonseed oil. No differences were found in behavior during winterization.

Determination of the component fatty acids by gas chromatography showed the fatty acid composition of the oils to be typical. Determination of the positions of the double bonds in the unsaturated acyl groups showed no differences between the oils from gland-containing, low-gland, and glandless seed. Ultraviolet, visible, and infrared spectra of the oils revealed no differences other than the presence of gossypol in the crude oil from the gland-containing seed. The infrared spectra of the unsaponifiable fractions obtained from the oils showed some differences, which were not believed to be important.

PIGMENT GLANDS, an anatomical peculiarity of cottonseed, contain the gossypol which adversely affects the economic utility of the seed. Unless the gossypol is inactivated or removed, the seed and the meal are toxic to nonruminants when fed at a sufficiently high dietary level. Small amounts of gossypol and its derivatives in crude oils contribute to the color problems, including color reversion, encountered with such oils. Obviously the development of a variety of cotton which is free of pigment glands is of tremendous economic importance.

Hopi cotton which belongs to the same species as commercial, North American upland cotton (*Gossypium hirsutum*) was reported by Lewton (7) and later by Fulton (6) to have variable numbers of pigment glands in the boll. S.C. McMichael of the U.S. Cotton Field Station, Shafter, Calif., is carrying out further experiments in this area (9). One variety of Hopi known as "Hopi Moencopi" or "Hopi M," has been crossed by McMichael to varieties or strains of upland cotton and selections having low-gland and glandless seed were made from later segregating generations. The transfer of the glandless seed characteristic to commercial varieties has been started. According to him no difficulties in the successful completion of such a transfer are apparent.

Several samples of low-gland and glandless cottonseed have been examined in the Southern Utilization Research and Development Division. A portion of one sample grown in 1958 was sent to Mattson and coworkers (8), who reported on the gossypol content and oil composition of the seed.

Because of the potential economic importance of this type of cottonseed, additional testing of the oil and meal from these seed is important. Breeding out the gossypol conceivably can introduce changes other than the elimination of gossypol. To conduct some of the further evaluation indicated, several new lots of seed were obtained. One was a low-gland and the other was a glandless seed, both grown in 1959. For comparison, commercial, gland-containing seed of the Acala 4-42 variety grown at the same location was obtained. Oil was extracted from these seed by cold-

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[1] Presented at the fall meeting, American Oil Chemists' Society, New York, N.Y., October 17–19, 1960.

[2] Trainee, Institute of International Education, UNESCO (present address: Union of Burma Applied Research Institute, Rangoon, Burma).

[3] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.