Surfactants Used in Textile Applications[1]

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Accurate statistics on surfactants used are difficult to obtain for various reasons. There are many different fabrics processed, each of which requires somewhat different processing. There are further differences in processing due to the properties desired in the final product, such as handle, color, and finish. Each mill has a somewhat different problem from that of other mills and so may use different processing methods. This makes extrapolation of figures obtained subject to error. The problems to be solved by each mill are constantly changing, resulting in a shift in type and quantity of surfactant used. Variations in the relative price of surfactants, particularly that of soap, often results in a change in the product used, particularly in wool scouring.

This introduction is a devious explanation why the data in this paper may be in error in some cases, and why a more detailed breakdown of some operations has not been made. It is hoped that this paper will at least constitute a start which can be expanded in the future.

The sources of data used in this paper are government statistics, requirements of individual textile mills, estimates made by textile supply houses, estimates made by manufacturers of surfactants, and published papers and books. It was encouraging to note that the partial estimates of detergent sales to the textile industry were reasonably close to the independently-arrived-at figure of mill requirements. The data to be presented are based on textile processing in 1952, the last year for which complete production data was available. Corresponding figures are given for 1953 where they are available.

One of the two determining factors of the amount of surfactant used in textile processing is the quantity of textiles processed. A start may be made with data for total textile production. These are shown in Table I.

TABLE I

Textile Production
(Millions of pounds)

Fiber	1952 Production	Consumption by End-Use	1953 Production (estimated)
Cotton	4,479	4,165	4,380
Wool			
Apparel	347	647	525
Carpet	120		
Rayon		1,469[a]	1,300[a]
Yarn	594		
Staple	212		
Acetate			
Yarn	234		
Staple	95		
Silk	7	6	7
Other			
Yarn	214	197	300
Staple	49		
Total	6,351	6,484	6,512

[a] Rayon and acetate combined.

The difference in production and consumption figures in the above table is due to one fiber being used as a relatively small part of a fabric consisting largely of another fiber. About 45 million lbs. of rayon and acetate, for example, were eventually sold in woolen goods. In addition, the consumption figure takes into account the reprocessed fibers. About 73 million lbs. of reprocessed wool were used in 1952.

The first simplification of the problem is made by noting that 3,279 million lbs. of the total 4,165 million lbs. of cotton consumed were used in broad woven goods. The rest of the cotton is used principally in knit goods, tire cord, cordage and twine, thread and tufted fabrics, none of which uses large quantities of surfactants in its processing. It is believed that the quantities of surfactants used in such operations are smaller than the probable error in the estimates to be made later, so these operations will not be included in this paper. The largest of these operations is knitting. Data on production are shown in Table II for those who may want to include it in other estimates.

The production of broad woven goods is shown in Table III.

TABLE II

Knitwear—1952 Production

Fiber	Millions of Pounds (estimated)
Cotton	190
Rayon and acetate	40
Wool	40
Nylon and other	25
Total	295

TABLE III

Production of Broad Woven Goods

Fabric	1952		1953	
	Millions of Yards	Millions of Pounds	Millions of Yards	Millions of Pounds
Cotton	9,515	3,279	10,203	3,295
Rayon and acetate	1,852	1,037	1,903	1,092
Wool	351		338	
Silk	42	8	38	8
Nylon	298	55	244	48
Other	122	96	120	97
Total	12,161		12,946	

The figures in Table III do not include tire cord or tire fabric. These are shown in Table IV, together with figures for 1950 which show that while the total production has remained relatively constant, the type of fiber used has shifted considerably.

The next step in the analysis of surfactant requirements is a breakdown of types of broad woven goods. The distribution for cotton is shown in Table V.

TABLE IV

Production of Tire Cord and Fabric
(In millions of pounds)

	1953	1952	1950
Cotton	73.2	139.0	226.0
Synthetic	447.8	392.0	297.0
Total	521.0	531.0	523.0

[1] Presented at the fall meeting of the Amercan Oil Chemists' Society, Minneapolis, Minn., Oct. 12, 1954.

TABLE V

Cotton Broad Woven Goods
(Millions of yards)

Type of Fabric	Total Yardage	Yardage Finished
		(estimated)
Duck	366	80
Narrow sheeting	1,750	1,220
Print cloth yarn	3,638	2,950
Colored yarn fabric	827	310
Wide fabric	667	190
Fine goods	1,113	1,660
Napped fabric	298	240
Towelling	428	420
Other	427	460
Total	9,515	7,530

Here again a simplification of the basic problem can be made. By far the largest part of the surfactants used goes into the production of fabrics that are bleached, dyed, or finished. Data on the quantity of fabric treated in these ways are published. The figures for cotton will be shown in Table VI. Through combination of these figures with mill surveys it is possible to estimate the quantity of fabric of each type which is so finished. These data are shown in Table V also.

TABLE VI

Cotton Goods Bleached, Dyed, or Finished

	Million Yards	Million Pounds
Bleached, white finished	3,380	990
Prepared, dyed and finished	2,410	700
Prepared, printed and finished	1,740	500
Total	7,530	2,190

In proceeding from these figures to those of Table VII, some of the more interesting parts must be concealed. This includes estimates of the weight per yard of each type of broad woven fabric and the subsequent calculations of the total weight of fabric passing through each process. These data were supplied for this paper by private communication. From estimates of the ratio of surfactants to fabric used in each processing step it is then possible to calculate the total quantity of surfactant used.

As an independent check, questionnaires were submitted to many textile mills and textile supply houses, inquiring into the products used and the approximate volume of use. It might be mentioned that replies differed considerably, reflecting the wide vari-

TABLE VII

Cotton Processing

Operation	Properties Desired[a]																												Surfactants Used[b]	Volume (millions of lbs.)	
	Anti-static	Detergency	Dispersing	Emulsifying hydrocarbons	Emulsifying mineral oils	Emulsifying natural oils	Effective in high salt conc.	Effective at high temp.	Effective at low temp.	Lubricating	Lime soap dispersing	Non-corrosive	Non-substantive	Oil-soluble	Rinsibility	Softening	Stable to acids	Stable to alkali	Stable to heat	Stable to hard water	Stable to metal ions	Stable to oxidizing agents	Stable to reducing agents	Substantive	Suspending	Very low foam	Wetting	Rewetting		Soap and Sulf. Oils	Syn-thetics
SPINNING	⊗				⊗					⊗		⊗		X										X		⊗			ape,ps,aa,toe	0.1	0.4
WARP SIZING																															
Emulsifier					⊗							X			X						⊗					X			SO,se	<0.1	<0.1
Penetrant			X				X																			X	⊗	⊗	AAS,so	0.1	0.4
Softener	X									⊗		X				⊗													ST,SO,S,se	18	<0.1
DESIZING																															
Acid		X	X														⊗		⊗							X	⊗		AAS,ape		0.4
Enzyme		X	X																							⊗	⊗		APE,AAS		
SCOURING		⊗				⊗					⊗				⊗	⊗		⊗							⊗		⊗		S,AAS,APE,so,fas,sa	0.3	0.5
BOILING		X				⊗												X							⊗	X	⊗				
Kier																													AAS,APE,so,sas,fas	0.1	0.2
Open																													S,AAS,SES,APE,sa,fas	0.2	0.5
BLEACHING						⊗			X	X								⊗				⊗			⊗	X	⊗		APE,AAS,fas,sa,ate		
Chlorine																															0.3
Peroxide																															0.6
MERCERIZING							⊗								X			⊗								X	⊗		Cresylic acid		
DYEING & PRINTING																															
Wetting out							X	X							X											X	⊗		DSS,AAS,sas,ape,ses		0.5
Dispersing			⊗					⊗							X			⊗							⊗	⊗	⊗		SES,FAE,AAS,ape, fas,sa,sas,se		3.6
Leveling			⊗					⊗										⊗					⊗		⊗	X	⊗				
STRIPPING			⊗															⊗					⊗		X		⊗		C, polyvinylpyrrolidone, ape		0.1
SOAPING OFF		⊗	X												X	⊗				X	X				⊗		X		FAS,APE,S,aas,sa,aa	0.2	0.8
FINISHING																															
Sanforizing	X									⊗						X											⊗		SES,so	0.1	0.3
Toweling																⊗											⊗	⊗	DSS,SAS		0.4
Softening	X															⊗								⊗					SO,FES,C,sa,toe	8.0	2.0
Resin Treatments																				⊗	⊗				⊗	X	⊗		AAS,fas,ape		0.1
																													Approximate Totals	27	11.5

[a] More important properties are shown encircled.
[b] In approximate order of use. Those in capitals are used in much greater volume than others.

ation among mills performing the same operation. There is as yet no "standard operating procedure."

Additional product and volume data were available through a survey of approximately 20% (by production volume) of cotton and synthetic finishing plants prepared recently for American Alcolac by its consultant, Luther B. Arnold.

These data for cotton are shown in Table VII. The surfactants used in each application have been listed in approximate order of volume of use. Those shown in capital letters are used much more extensively than those in lower case letters. To conserve space an abbreviation has been used for each type of surfactant. The key to the abbreviations is given in Table VIII. It should be noted that no attempt has been made to break down the types of soap used though there are almost as many different soaps as there are synthetic surfactants.

All volume figures are given on an active-agent basis. Those for soap and sulfonated oils are calculated on the estimated equivalent of synthetic surfactant that would be used.

To assist the research chemist in preparing surfactants for textile applications the desired properties for each process are also shown.

Among interesting items pointed up by Table VII are the large number of different types of surfactants used and the fact that softeners and lubricants far exceed in volume the detergents and penetrants.

A similar analysis has been made for surfactants used in wool processing. This is given in Table IX.

TABLE VIII

Surfactant Types

Class Name	Typical Products	Symbol
Anionic		
Soap		S
Alkylarylsulfonates	Nacconol, Nekal	AAS
Fatty alcohol sulfates	Duponol, Sipex	FAS
Secondary alkyl sulfates	Tergitol 08	SAS
Dialkyl sulfosuccinates	Aerosol, Decersol	DSS
Sulfonated amides	Igepon	SA
Petroleum sulfonates	Petronate	PS
Sulfated ethers	Triton X200	SET
Sulfated esters	Alcowet RS, Nopco 1285	SES
Sulfonated oils		SO
Sulfonated tallow		ST
Sulfonated glycerides		SG
Nonionics		
Alkylphenol ethers	Triton X100, Igepal CO	APE
Tall oil esters	Renex, Sterox CD	TOE
Fatty acid ester	Energetic	FES
Alkyl thioethers	Nonic 218	ATE
Alkylolamides	Ninol, Alrosol	AA
Polyoxyalkylene ethers	Pluronics	PE
Fatty alcohol ethers	Brij	FAE
Sorbitan esters	Span	SE
Cationic		C

The symbols used here are the same as those used previously.

While the data presented on cotton and wool can at least be dignified by the term "estimates," that for the synthetics must be considered closer to educated guesses. Production figures for these fibers are shown in Table X. The weights of the fibers have been shown in Tables I and II.

The quantities of fiber passing through each processing application are not easily estimated from this data for synthetics so that greater reliance was

TABLE IX

Wool Processing

Process	Desired Properties																												Surfactants Used	Volume (millions of lbs.)	
	Anti-static	Detergency	Dispersing	Emulsifying hydrocarbons	Emulsifying mineral oils	Emulsifying natural oils	Effective in high salt conc.	Effective at high temp.	Effective at low temp.	Lubricating	Lime soap dispersing	Non-corrosive	Non-substantive	Oil-soluble	Rinsibility	Softening	Stable to acids	Stable to alkali	Stable to heat	Stable to hard water	Stable to metal ions	Stable to oxidizing agents	Stable to reducing agents	Substantive	Suspending	Very low foam	Wetting	Rewetting		Soap & Sulf. Oils	Synthetic
Raw wool scouring		⊗				⊗			X		⊗		X		⊗	⊗		⊗	X						⊗				S,APE,aas,toe	0.7	1.2
Oiling	⊗				⊗	⊗						⊗		⊗	X											X			PS,SO,SG,ape	0.6	<0.1
Backwashing		⊗				⊗									⊗			X							⊗				S,sa,ape	0.1	<0.1
Yarn scouring					⊗								⊗		⊗			X											APE,S,AAS,toe	0.3	0.5
Carbonizing					⊗	⊗	⊗				X						⊗		⊗								⊗	⊗	AAS,ape,c,aa		0.25
Sizing																										⊗	⊗				<0.1
Desizing																	⊗								⊗	X	⊗				<0.1
Cribbing					⊗																				⊗		⊗		SA,AAS		0.2
Piece scouring		⊗			⊗	⊗			X		⊗		X		⊗			⊗											S,APE,aas,toe,sa,fae	0.5	0.7
Fulling		X								⊗	⊗					X	⊗								⊗				S,aa,sa,fas,ape	>5.0	0.6
Bleaching															⊗			⊗				⊗				⊗	⊗		APE,sa,aas		0.1
Dyeing			⊗					X							X	⊗	⊗				⊗				⊗	X	⊗				2.3
Acid																													AAS,aa,fas,dss,C		
Chrome																													FAE,aas,c		
Other																													C,pe		
Stripping																							⊗		⊗		⊗				0.1
Shrinkproofing																		⊗				⊗					⊗				<0.1
Mothproofing				⊗																					⊗		⊗		ape		<0.1
Softening																⊗								⊗					C,SO	0.2	0.3
																													Approximate Totals	>7.5	7.0

TABLE X
Production of Synthetic Broad Woven Fabric
Millions of Linear Yards
(1952 Preliminary)

Operation	Rayon and Acetate		
	Rayon [a]	Acetate [a]	Total
Bleached and white finished	107	50	157
Dyed and finished	1,066	490	1,556
Printed and finished	143	70	213
Total			1,927

Operation	Nylon	Silk	Other	Total
Bleached and white finished	61	2	6	226
Dyed and finished	196	15	21	1,788
Printed and finished	41	19	4	277
Total	298	36	31	2,291

[a] Division estimated from production.

placed on extrapolated values obtained from selected mills. Table XI shows the surfactants used in the various operations. In several cases no estimate of any kind could be made on the basis of the data available in time for presentation of this paper.

Because of the limited data available it has been necessary to offer it in the above form. It must be emphasized however that there is a considerable variation in many of the processes grouped under headings such as "dyeing" or "scouring." There are several different types of equipment in use for such operations, and often a surfactant superior in performance in one type of equipment will not be the choice for another.

Since an estimate of the quantities of each surfactant used in textile industry would undoubtedly be of interest, an analysis is shown in Table XII. It should be noted however that these figures are guesses made from estimates and so may be considerably in error.

One of the sticky problems encountered is that of determining just what surfactants should be classed as synthetic since all of them are conversion products and thus may be considered to be made synthetically. In this survey the soaps, petroleum sulfonates, and sulfonated fats and oils were considered separately. The totals for these products are probably less accurate than those for the products more commonly considered synthetic surfactants. The total for soaps, petroleum sulfonates, and sulfonated fats and oils is estimated to be about 43 million lbs., of which about 30 million lbs. are used as softeners.

As mentioned previously, surfactants in textile applications are still in a period of adjustment. There is an almost constant displacement of one type of product by another. Some stability exists however as several surfactants won markets in the textile industry by being there first. If they perform reasonably well, they hold their market even if technically superior or less expensive products are offered later. Their position is further solidified by the fact that the cost of evaluating a new surfactant properly is expensive; one large mill estimates the cost at $200 per sample for laboratory testing only. With so many surfactants to choose among, the possible benefits to

TABLE XI
Processing of Synthetics

Process	Desired Properties																												Surfactants Used	Viscose	Acetate	Nylon	Other
	Anti-static	Detergency	Dispersing	Emulsifying hydrocarbons	Emulsifying mineral oils	Emulsifying natural oils	Effective in high salt conc.	Effective at high temp.	Effective at low temp.	Lubricating	Lime soap dispersing	Non-corrosive	Non-substantive	Oil-soluble	Rinsibility	Softening	Stable to acids	Stable to alkali	Stable to heat	Stable to hard water	Stable to metal ions	Stable to oxidizing agents	Stable to reducing agents	Substantive	Suspending	Very low foam	Wetting	Rewetting					
Xanthation			X						•	X								⊗								X	⊗		SO	0.3	—	—	—
Anticratering	X		⊗														⊗	⊗								X			C,ape,pe	0.8	—	—	—
Desulfuring		X	⊗												X										⊗				AAS,sa,fas	1.0	—	—	—
Yarn lubrication	⊗					⊗				⊗					⊗				X							X		⊗	SO,SES,S,fae	3.5	4.0	—	0.1
Sizing																																	
Penetrant															X						X					X	⊗		ape,aas	<0.1	<0.1	—	—
Softener	⊗									⊗		X				⊗													ST,SO	1.5	—	—	—
Emulsifier				⊗																					⊗				fas,aas,ape	—	—	<0.1	<0.1
Desizing		⊗	⊗																										ape	<0.1	—	—	—
Bleaching			X																			⊗			X		⊗		AA	<0.1	—	—	—
Boil-off		⊗	X												X												⊗		AA,ape	<0.1	—	—	—
Dyeing & Printing			X				⊗	⊗								⊗					⊗				⊗	X	⊗		FAS,FAE,ape, aa,aas,sa,pe	1.2	0.8	0.6	0.2
Soaping		⊗	X												X	⊗					X				⊗				APE,SA,FAS,	2.0	1.5	1.0	0.3
Delustering			⊗		⊗									⊗											⊗				AA,s C,fae,fes	<0.1	0.1	—	—
Softening																																	
Permanent																⊗								⊗					C	0.5	0.3	0.2	0.1
Non-permanent																⊗													SO,ST	0.2	0.1	—	—
Anti-static	⊗																							X					C	—	—	0.2	—
Resin finishes																⊗											⊗		C,aas,fas,ape	0.2	0.2	0.1	v.s.
Soap, etc. 9 / Synthetics 14.5 / Approximate Total 23.5																														12.8	7.8	2.4	0.5

TABLE XII

Surfactants Used in Textile Applications
(Millions of pounds of active agent)

Anionics		
Alkylarylsulfonates	6.0	
Sulfated esters and ethers	4.0	
Fatty alcohol sulfates	2.5	
Sulfonated amides	2.5	
Sulfosuccinates and secondary alkyl sulfates	1.0	
Others	0.5	
Total		16.5
Nonionics		
Alkylphenol ethers	7.0	
Fatty alcohol ethers	2.0	
Alkylolamides	1.5	
Tall oil and fatty acid esters	1.5	
Others	0.5	
Total		12.5
Cationics		4.0
Grand Total		33.0

be obtained from a new product are worth less than the cost of evaluating the surfactants. Nevertheless extensive surfactant testing is being carried out in many of the larger mills. Some of the factors which will cause further shifts in the selection of surfactants are: the steadily decreasing price of the nonionics, the increasing proportion of fabric that receives special finishing operations, the increase in the production of nylon and other synthetics, the decrease in the production of acetates, the displacement of cotton by synthetic fibers in tire yarn, and the displacement of kier boiling by the open boil-out.

Other definite trends are the rapid displacement of soap by synthetics in scouring after dyeing and printing, the displacement of sulfonated oils by cationics in finishing, and the rapid increase of nonionic usage.

There is one further point to be noted by research chemists in preparing surfactants for the textile industry. Although this industry consumes very large quantities of chemicals, it is not primarily one of the chemical processing industries. It is a mechanical industry, concerned with the conversion of materials of one physical form to another. The chemicals are used as auxiliaries to facilitate these mechanical operations. They may be used to lubricate the fiber to make it spin better or to color the fabric to make it more attractive or to coat the fabric to change its handling properties, but the basic operations are still mechanical. The investment in money and know-how in these mechanical operations is tremendous. It does no good therefore to develop a surfactant that is excellent under some theoretical set of conditions. The surfactant is the tail of the dog. It must be designed to work best under the conditions that exist.

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Chemical Determination of Unsaturation of Fats and Derivatives

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THIS PAPER is a summary progress report on the chemical determination of unsaturation of fats and derivatives. Special emphasis is placed on recent studies and the current status. The determination of unsaturation of vegetable oils has been studied for a very long time. The importance of unsaturation in determining the characteristics of oils and fats is well recognized. For example, vegetable oils are sometimes characterized as nondrying when the iodine value is below 120, semi-drying when between 120 and 160, and drying when above 160. Their use and value depends to a large extent upon their unsaturation.

The usual procedure for determining the degree of unsaturation is to measure the amount of halogen that may be added to the double bond. The chemistry involved is very simple. Two halogens, not necessarily the same, attach themselves to the two carbons involved in the unsaturation. These halogens may be chlorine, bromine, or iodine. The general procedure is to add an excess of the halogen and determine the amount used by measuring the amount of halogen left after the reaction. The trick is to arrange conditions so that quantitative addition takes place without the substitution for one of the hydrogens.

The degree of unsaturation is expressed as the grams of iodine added to 100 g. of material, or the equivalent centigrams of iodine per gram of sample. This brings up one point of controversy among the oil chemists. Should this constant be called iodine value or iodine number? The older literature seems to prefer iodine number while more recently iodine value is obtaining wide usage. A.O.C.S. methods use iodine value while American Society for Testing Ma-