The location variability was shown to be closely associated with maximum temperature during seed development. Temperature appears to be the most important environmental factor affecting these acids, especially linolenic.

The percentages of the two acids are positively correlated with each other.

REFERENCES

1. Alderks, O. H., J. Am. Oil Chemists' Soc., *26*, 126–132 (1949).
2. American Oil Chemists' Society, Official and Tentative Methods, revised, 1951.
3. Anonymous, Soybean Digest, *17*(5), 26 (1957).
4. Collins, F. I., and Sedgwick, V. E., J. Am. Oil Chemists' Soc., *33*, 149–152 (1956).
5. Dutton, H. J., Lancaster, C. R., and Brekke, O. L., J. Am. Oil Chemists' Soc., *27*, 25–30 (1950).
6. Howell, R. W., and Cartter, J. L., Agron. J., *45*, 526–528 (1953).
7. Howell, R. W., and Collins, F. I., "Factors Affecting Fatty Acid Content of Soybean Oil," Agron. J., in press.
8. Mattil, W. H., Oil and Soap, *21*, 197–201 (1944).
9. Morse, W. J., Cartter, J. L., and Williams, L. F., U. S. Dept. of Agric., Farmers' Bull. 1520, revised, 1949.
10. Powers, P. O., Oil and Soap, *22*, 52 (1945).
11. Scholfield, C. R., and Bull, W. C., Oil and Soap, *21*, 87–89 (1944).
12. Simmons, R. O., and Quackenbush, F. W., J. Am. Oil Chemists' Soc., *31*, 601–603 (1954).
13. Snedecor, G. W., "Statistical Methods," Iowa State College Press, Ames, Ia., 4th ed., 1946.
14. Sreenivasan, B., and Brown, J. B., J. Am. Oil Chemists' Soc., *33*, 521–526 (1956).
15. U. S. Weather Bureau, Climatological Data, 1955.

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The Effect of Builders on the Sorption of Sodium Myristyl Sulphate on Cotton and on Carbon

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THE BENEFICIAL EFFECT of builders on the detergent efficiency of soaps and synthetic detergents is well known, but as yet no completely sastisfactory theory of builder action has been proposed. It is believed that the sorption of detergent ions by both soil and fabric plays an important part in the mechanism of detergency although the precise relationship between sorption and detergency has not been established (4,11). The present work was undertaken in the hope that some further clarification might be obtained of the mechanism of builder action and/or of the role of sorption in the detergent process.

Data have already been presented relating to the sorption of various soaps and synthetic detergents on carbon black (7, 8, 13) and on textile fibers (12, 14). While builders in general were not included in this work, it was shown that the addition of sodium sulphate to solutions of synthetic detergents led to an increase in the sorption of the detergent in all cases (8, 12). The sorption of synthetic detergents on various textile fibers was also found to be influenced by the pH of the solution; the sorption of anionic detergents was greater in acid than in alkaline media (3, 12).

Meader and Fries (4) noted that the addition of salts to a solution of sodium alkybenzene sulphonate increased the sorption of the latter on cotton. Sodium sulphate was more effective than tetrasodium pyrophosphate.

Boyd and Bernstein (1), on the other hand, have recently reported that the addition of builders, including sodium sulphate, sodium carbonate, and various phosphates, to solutions of sodium dodecylbenzene sulphonate decreased the sorption of the latter on cotton and on various synthetic soils. Their data however do not refer to equilbrium sorption but rather to the amount of sorbed material remaining after a specified rinsing procedure.

Schneider (10) has studied the heats of immersion of a carbonaceous soil in built detergent solutions and has concluded that builders increase the rate of sorption of the detergent. Those builders which have a high anionic charge were most effective.

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Materials and Methods

Sodium myristyl sulphate was prepared by the method of Dreger *et al.* (2) and was recrystallized several times from absolute alcohol. The melting point was 182–3°C., and the infrared spectrum was free of bands in the hydroxyl region.

The builders used are listed in Table I. The phosphate builders were obtained from Electric Reduction

TABLE I
Builders Used

Compound	Abbreviation	Anionic charge	pH of 1% solution	Analysis
Sodium metasilicate	S M	−2	12.3	Na_2O–29.4%; SiO_2–29.2%
Trisodium phosphate	T S P	−3	12.1	18.6% as P_2O_5
Tetrasodium pyrophosphate	T S P P	−4	10.3	53.2% as P_2O_5
Sodium tripolyphosphate	S T P P	−5	9.8	57.5% as P_2O_5
Sodium hexametaphosphate	S H M P	−6	7.6	64.2% as P_2O_5
Sodium carbonate, anhydrous	Na_2CO_3	−2	10.6	Reagent grade [a]
Sodium sulphate, anhydrous	Na_2SO_4	−2	6.7	Reagent grade [a]

[a] Conforms to A.C.S. specification.

Sales Company Ltd., Buckingham, Quebec, and the silicate from National Silicates Ltd., Toronto, Ontario.

The carbon black was uncompressed Standard Micronex, supplied by the Binney and Smith Company, New York. The cotton was a fully-bleached nainsook fabric supplied by Tootal and Broadhurst Lee Co., Manchester, England, and was prepared as described previously (14).

The sorption of sodium myristyl sulphate on cotton was determined at 50 ± 2°C. by the method described previously (12) except that the weight of cotton used for each determination was increased to 10 g. and the volume of solution was decreased to 100 ml. The initial solutions contained 0.1% of sodium myristyl sulphate and 0–0.2% of the various builders.

The sorption on carbon was determined at 50 ± 2° C. as in previous work (8) except that the volume of solution used was 100 ml. instead of 150 ml. In the first trials a concentration of 0.1% sodium myristyl sulphate was used, but difficulty was encountered in filtering the equilibrium solution. It had been noted previously (8) that suspensions of carbon black in detergent solutions at concentrations below the critical micelle concentration filtered readily, but when the concentration was above the c.m.c., carbon tended to pass through the filter paper. Since the c.m.c. for sodium myristyl sulphate is approximately 0.002*M* (8) or 0.06%, for this portion of the work the initial solutions were made up to contain 0.05% sodium myristyl sulphate and 0–0.4% of the various builders. These suspensions filtered readily. All determinations were carried out in duplicate and many in triplicate.

Data and Discussion

Sorption on Cotton. The data for the sorption of sodium myristyl sulphate on cotton are given in Figure 1. In spite of considerable scattering of the experimental points it would appear that there is an approximately linear relationship between detergent sorption and builder concentration. Consequently the best straight lines through the points were calculated by the method of least squares and are shown in Figure 1. It is apparent that there is a small but significant increase in the sorption of detergent with increasing builder concentration in all cases and that the less alkaline builders cause the greatest increase in sorption (Figure 1, Table I).

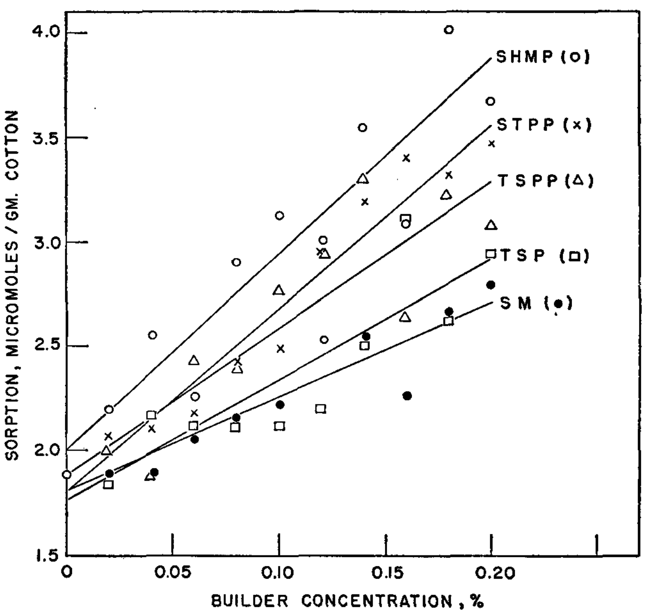

FIG. 1. Sorption of sodium myristyl sulphate from 0.1% solution at 50°C. on cotton.

It has been shown previously (12) that the sorption of sodium myristyl sulphate on cotton is less in alkaline than in acid solution. This was attributed to an increase in the negative charge on the cotton with increasing pH (5) resulting in a corresponding increase in electrostatic repulsion between fiber and detergent anion. These findings are substantiated by the present work to the extent that the less alkaline builders caused the greatest increase in sorption of detergent. On the other hand, all of the builders, with the possible exception of S H M P, are more alkaline than the detergent itself, and yet an increase in sorption in the presence of builder was noted in all cases. This suggests that the effect of builders on sorption is the resultant of two opposing tendencies, *viz.*, a) the effect of the pH of the solution, which in the case of alkaline builders tends to decrease the sorption, and b) the effect of the builder anion, which tends to increase the sorption.

It has been suggested (6, 9) that builder action in detergency is the result of sorption of the builder anion on the soil and/or the fabric with a consequent modification of the electrical charge relationships. This view was not substantiated by the present findings, since in one case, that of sodium myristyl sulphate + T S P, there was no measurable sorption of the builder anion on the cotton (Table II). This has

TABLE II

Sorption of T S P on Cotton in the Presence of 0.1% Sodium Myristyl Sulphate

T S P concentration %	PO_4^{---} concentration, p.p.m.	
	Initial solution	Final solution
0.08	199	209
0.09	234	238
0.10	260	265

also been confirmed by Schneider (10) with respect to the sorption of various builders on carbon.

The ability of builders to increase the sorption of surface-active compounds is attributed by Schneider (10) to an increase in the rate of sorption. He suggests, in accord with our previously expressed views (12), that unassociated detergent anions are sorbed but that micelles are not sorbed. When sorption takes place at concentrations above the c.m.c., micelles dissociate to replace the single ions which have been removed by sorption. Thus the rate of micelle dissociation controls the rate of sorption. Schneider suggests that builders, by virtue of their anionic charges, tend to distort the gegenion sheath surrounding the micelle and hence increase the rate of micelle dissociation. Those builders which have the highest anionic charge are therefore the most effective in increasing rate of sorption. While the data obtained in the present work are not sufficient to permit their use in a critical evaluation of this theory, it is apparent that the results for sorption on cotton do not contradict it.

Sorption on Carbon. The data for the sorption of sodium myristyl sulphate on carbon are given in Figure 2. The rapid increase in sorption at comparatively low builder concentrations suggests that these curves are exponential in form, and this was confirmed by plotting the data on logarithmic scales. The curves obtained were essentially linear.

In the absence of builder the sorption on carbon is much higher than that on cotton, as might be expected

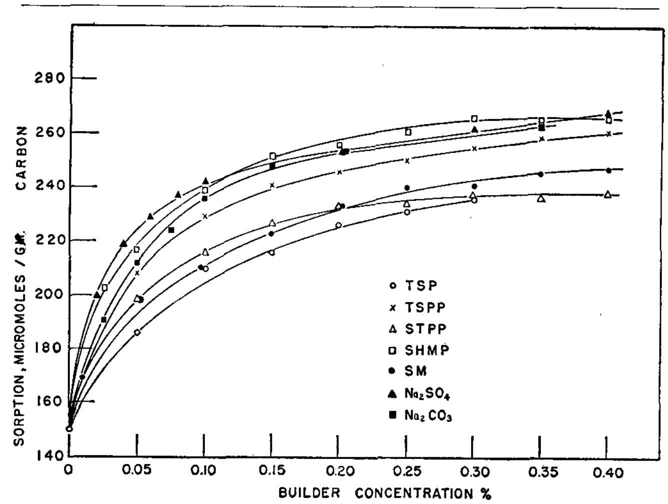

FIG. 2. Sorption of sodium myristyl sulphate from 0.05% solution at 50°C. on carbon.

from the difference in surface area of the two materials. (Vold and Phansalkar [11] give 1.64 m^2/g. for the specific surface of a cotton sheeting probably similar to that used in the present work, and the surface area of the carbon is given as 95 m^2/g. [15]). While the average level of sorption is much higher on carbon than on cotton, the difference between builders is less marked. For example, at 0.2% builder concentration, the highest sorption obtained on cotton (with S H M P) was about 43% higher than the lowest sorption (with T S P) whereas the corresponding figure for sorption on carbon was only about 14%. Within this comparatively narrow range there is considerable crossing of the curves so that it is not possible to establish any clear-cut order of effectiveness of the builders. It should be noted however, that at the highest sorption levels, *e.g.*, with 0.4% S H M P, about 90% of the available detergent has been sorbed. If a higher initial concentration of detergent had been used, it is possible that a greater differentiation between builders might have been obtained, *i.e.*, the maximum sorption is probably limited less by the action of the builder than the amount of detergent available for sorption.

Schneider's theory (10) that builder action is caused primarily by an increase in the rate of micelle dissociation is not substantiated by the data for sorption on carbon. The concentration of detergent was in all cases below the c.m.c., yet substantial increases in sorption were observed in the presence of builders. Furthermore it has been shown previously (8) that under the experimental conditions employed, equilibrium is established in less than 10 min. Hence an increase in the rate of sorption, unless also accompanied by a change in the equilibrium conditions, would not be expected to increase the total amount sorbed in 10 min. or longer. It is therefore concluded that, while an increase in the rate of micelle dissociation may be a contributing factor in those cases where it is applicable, the mechanism of builder action cannot be explained satisfactorily on this basis alone.

Summary

In the case of sorption on cotton there was an approximately linear increase in sorption of the detergent with increasing builder concentration. The effectiveness of the builders in this respect increased with increasing anionic charge and decreasing pH of the builder. In the case of sorption on carbon the addition of builder again led to an increase in sorption, but in this case the sorption was an exponential function of the builder concentration. The differences in effectiveness of the various builders in increasing sorption was less clear-cut than in the case of sorption on cotton, and there did not appear to be any consistent correlation between the amount of detergent sorbed and either the pH or the anionic charge of the builder.

REFERENCES

1. Boyd, T. F., and Bernstein, R., J. Am. Oil Chemists' Soc., *33*, 614–619 (1956).
2. Dreger, E. E., Keim, G. I., Miles, G. D., Shedlovsky, L., and Ross, J., Ind. Eng. Chem., *36*, 610–617 (1944).
3. Flett, L. H., Hoyt, L. F., and Walter, J., Am. Dyestuff Reptr., *41*, P139–143 (1952).
4. Meader, A. L., and Fries, B. A., Ind. Eng. Chem., *44*, 1636–1648 (1952).
5. Neale, S. M., and Peters, R. H., Trans. Faraday Soc., *42*, 478–487 (1946).
6. Powney, J., and Noad, R. W., J. Textile Inst., *30*, T157–171 (1939).
7. Reade, M. A., Weatherburn, A. S., and Bayley, C. H., Can. J. Research, *F27*, 426–428 (1949).
8. Rose, G. R. F., Weatherburn, A. S., and Bayley, C. H., Textile Research J., *21*, 427-432 (1951).
9. Sanders, H. L., and Lambert, J. M., *ibid.*, *21*, 680–684 (1951).
10. Schneider, C. H., Ph.D. thesis, Lehigh University (1955); Dissertation abstr., *15*, 1509 (1955).
11. Vold, R. D., and Phansalkar, A. K., Rec. trav. chim., *74*, 41–51 (1955).
12. Weatherburn, A. S., and Bayley, C. H., Textile Research J., *22*, 797–804 (1952).
13. Weatherburn, A. S., Rose, G. R. F., and Bayley, C. H., Can. J. Research, *F27*, 179–193 (1949).
14. Weatherburn, A. S., Rose, G. R. F., and Bayley, C. H., *ibid.*, *F28*, 51–61 (1950).
15. Weatherburn, A. S., Rose, G. R. F., and Bayley, C. H., *ibid.*, *F28*, 213–225 (1950).

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A Disk Rheometer Applicable to Measuring Shortening Flow-Properties

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THE RESOLUTION of the physiological concept of shortening "consistency" in a numerical system is a challenging problem. Shortening systems, being transitory in nature susceptible to changes by temperature, time, shear, and other variables, are not simple rheological systems to study. Some of the properties of shortenings have been measured by various applications of viscometry. Gravenhorst (4) applied a Brinnell type of ball penetrometer, using a relatively constant shear rate and measuring the stress variable. Clardy *et al.* (1) developed another version of the constant shear rate-variable stress approach by using an orifice and ring forced through the sample. The techniques of Rich (6), using the A.S.T.M. Grease Penetrometer, and of Feuge and Bailey (3), using the micropenetrometer test, are modifications of a constant-stress, variable-strain principle.

These tests contribute greatly to the measurements of shortening consistency but are limited to the application of one shearing action. Recognizing that shortenings are subject to changes by shearing or "working" and that the system is temperature-dependent, test equipment was designed and a method was developed which would determine the relative viscosities of shortenings under a single shear application; the change in viscosities of shortenings as a result of controlled repeated shearing or working; and the relationships of both of these properties as a function of temperature.

In addition to these fundamental objectives, consideration was given to sample dimensions so to facilitate sampling of pails, drums, cartons, and similar unit-sizes. The aspect of laboratory preparation of shortenings was not overlooked, and the sample shape was made compatible with laboratory chilling-techniques. Operator convenience and the speed of the test were studied to achieve the compromise of maximum test output per man-day and maximum interpretation. The method and equipment was designed