A Detergency Test Based on Rapid Aging of Unremoved Sebum

W. G. SPANGLER, R. C. ROGA and H. D. CROSS III, Colgate-Palmolive Company, Jersey City, New Jersey

Abstract

A laboratory test has been developed for screening detergent compositions with respect to the removal of sebum soil in the absence of particulate soil. The fabrics are uniformly soiled with an aqueous emulsion of synthetic sebum and are then laundered under controlled conditions in a Terg-o-Tometer. The unremoved soil is rapidly aged, and the resulting yellowness is measured instrumentally.

This test can be run in a minimum amount of time and with a minimum amount of equipment. It enables one to check many variables (such as sequestering capacity, temperature effects, brightener build-up under soiled conditions, etc.) on various fabrics, with or without special treatments. The results are in terms of yellowness, which is recognized by the housewife, and are not a measurement of total soil removal. These values, when combined with grayness values derived from the sebum airborne test, are good prognosticators of practical performance.

Introduction

THIS PAPER is the third of a series of screening tests presented on the evaluation of detergent compositions (1, 2). In each test method, synthetic sebum was used as the fatty soil. The first procedure measured foam in the presence of sebum, the second was a measure of airborne particulate removal when used with sebum as a soil, and this paper is a measure of the removal of sebum itself in terms of yellowness. Washing conditions have been maintained very close to those of practical laundering so as to measure foam, grayness, and yellowness as developed in the home.

Utermohlen et al. (3) believed that the removal of solid soil and of oily soil are separate phenomena and are not related to any great extent. A pro and con discussion of this topic by two experimental teams working with electron microscopy equipment is found in the work by Howarth et al. (4). Studies relating to fatty soil removal by using radioactive tracers have been reported by Wagg and Britt (5), Scott (6), Gordon (7), and Gilderson (8). Powe (9) and Oldenroth (10) used gravimetric procedures for studying skin soil removal. Huggins (11) and Clayton (12) are engaged in detergent studies and are using synthetic sebum as the oily soil.

The formation of yellowness on fabrics has been studied by McLendon and Richardson (13, 14), Wagg et al. (15), and Loeb (16). Privett (17) made a study of the yellowing of oil films.

In observing soiled laundry, one notes that pillow cases, shirt collars, T-shirts, sheets, etc., develop a yellow color after repeated launderings or prolonged storage (Fig. 1). This is attributed in part to the oxidation and polymerization of certain fractions of the body oils which have not been removed during washing. However it is not the sole cause. The nature of the fabric, various treatments applied to the fabric, excess alkali, bleaching effects, etc., all can be contributing factors. This paper deals essentially with yellowness attributable to residual synthetic sebum. In particulate removal, the green reflectance is measured which relates to grayness. This reflectance is dependent on particle size, chemical composition, geometry, etc., and relates more to the effect of the soil rather than the amount. If, in natural soiling, the particulate is a white metallic oxide or silicate, it could have a beneficial effect as compared with a light absorbing surface, such as carbon or black metallic oxides. Yellowness always detracts from white as does grayness, but it usually detracts about three to four times as much. Again, all the components of sebum do not produce yellowness (measured by the blue reflectance). Thus in this work the attempt is to measure only the undesirable effects of the residuum.

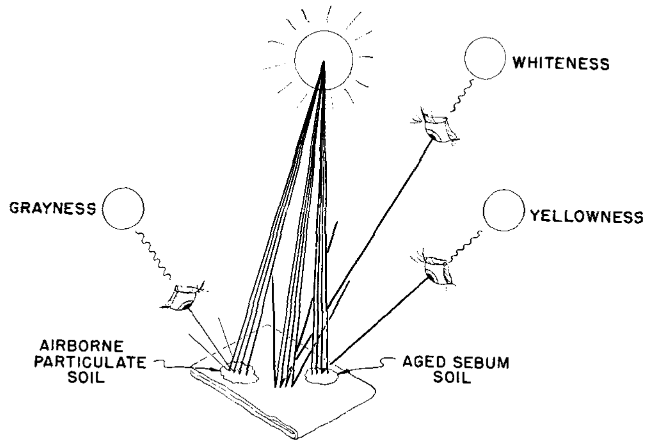

FIG. 1. What the housewife sees.

Experimental Section

Apparatus

Terg-o-Tometer
Laboratory padder
Shaking device—"Charfish" shaker (Figure 2), de-

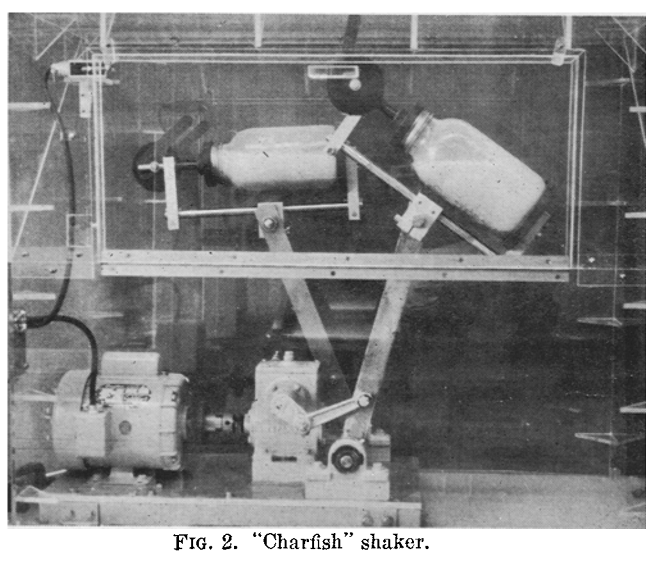

FIG. 2. "Charfish" shaker.

signed by Charles Fischer, Colgate, R&D.
Drying equipment optional: print dryer, clothes dryer, or scorch tester.
Color difference meter

Reagents

Synthetic sebum (1)
Representative fabrics

Procedure

Regular synthetic sebum or modified synthetic sebum is applied to the pretreated fabric as an aqueous emulsion by means of the Charfish shaker. The swatches of fabric are dried at a low heat (140–160F), then washed under various conditions in the Terg-o-Tometer. Aging is usually carried on by heating the fabric at some temperature between 200–300F for approximately an hour. The developed yellowness is measured on a color difference meter (18).

1) Preliminary work was done with synthetic sebum applied to the fabric and aged without washing. This permitted exploration of the various factors which enter into the yellowing of soiled clothing before laundering. The fabrics used were obtained from Testfabrics Inc. (Indianhead cotton, Nylon 66-spun 354 A, and Dacron 54, spun 754 AW). They are unreal in the sense that they do not represent material used in finished goods (no brighteners, finishes, etc.) but real as far as chemical composition is concerned.

Wagg (15) soiled cotton with 4–5% petroleum spirit solution of sebum components and washed them in soap and alkali at 104F. They were then oven-heated. He concluded that, of the three components tested, squalene and linolenic acid caused yellowing whereas cholesterol did not. McLendon and Richardson (13) tested six components of sebum at low and high relative humidity. They concluded that cholesterol was the only additive at low relative humidty which gave an increase of more than one "b" unit.

At high relative humidity most of the compounds yellowed the fabric. The unsaturated compounds caused more yellowing than the saturated compounds, and cholesterol caused more yellowing than cetyl alcohol. Experimental work as reported in this paper consisted of treating the three types of fabric with 2% emulsions of each of seven ingredients of sebum. These were aged in a clothes dryer at a mean temperature of 217F for one hour (Table I).

The swatches were shaken twice with the Charfish shaker and padded twice. Although the amount of wet pick-up was different, the dried swatches showed between 4.5–5.0% sebum soil, based on the weight of the fabric. The data show that Nylon is affected most by an increase in temperature and has the most yellowness in the original. These factors must always be considered when making cross-comparisons on sebum removal. Cottonseed oil was included because it may be used in future synthetic sebum formulas.

It can be readily seen that not all fabrics are yellowed to the same degree by the same agents. Franks (19) concluded that the oxidation of ethyl linoleate on a cotton substrate is more rapid than the corresponding reaction in the bulk-ester phase. This appears to be caused by the limited stability of the hydroperoxide on the cotton substrate. He further stated that some of the oxidation products undergo a slow reaction with the substrate, resulting in a partial insolubilization of the yellow compounds. There could also be a possible reaction between the polyamide and the sebaceous material. Rochas (21) stated that the yellowing of the Nylon fiber on account of a temperature rise is connected with the formation of pyrrole rings.

2) Since linoleic acid was the most effective yellowing agent and since O'Neill (20), Wagg (15), and McLendon (14) have reported the effect of nitrogenous products on yellowing, modified sebums with excess linoleic acid or excess amine soap were tested as in Part 1. Table II shows the relationship between the original fabric, the aged original fabric (one hour in clothes dryer at mean temperature of 190F), the original fabric plus sebum, the aged original fabric plus sebum, the aged fabric with sebum plus double the amount of emulsifying agent, and the aged fabric with sebum plus 10% additional linoleic acid.

It is interesting to note that doubling the amine soap caused an increase of 3 "b" units on cellulose at this temperature but only about 0.4 "b" unit on the synthetics. The additional linoleic acid increased the yellowness on cellulose by approximately 5.6 "b" units over regular sebum and by about 6 "b" units on polyamide. The 1.2 "b" unit on the polyester is comparatively small. Privett et al. (17) have investigated the yellowing involved in oil films and have concluded that two distinct steps are involved: a) the formation of colorless precursors by an oxidative process, and b) the reaction of the precursors to give the yellow compounds.

It was previously believed by the authors that it might be better to emulsify the sebum without the aid of an agent, such as an amine soap. However, since natural perspiration contains nitrogenous products

TABLE I
Percentage of Sebum Pick-up and Yellowness Developed by Individual Ingredients

	Weight of originals	Weight of padded swatches		Percentage of emulsion	Percentage of sebum
		Wet	Dry		
Cellulose	18.3 g	32.2	19.2	75.9	4.9
Polyamide	11.4 g	17.5	11.9	53.5	4.4
Polyester	10.5 g	15.0	11.0	43.0	4.8

"b" Units

	Cellulose	Polyamide	Polyester
No agent	2.5	6.8	3.8
Linoleic acid	17.0	20.9	6.4
Cottonseed oil	9.0	14.4	8.0
Cholesterol	9.0	10.2	7.9
Oleic acid	8.2	13.2	5.6
Olive oil	7.1	11.2	4.8
Squalene	6.7	10.8	3.8
Coconut oil	4.9	8.9	4.0

TABLE II
Effect of Nitrogenous Material and Unsaturated Fatty Acids on Yellowing

	"b"		
	Cellulose	Polyamide	Polyester
Original	2.2	2.2	1.8
Aged original	2.7	3.4	1.9
Original + sebum	3.2	2.2	1.9
Original (aged) + sebum	8.0	4.8	2.3
Original + sebum + 2x emulsion (aged)	11.0	5.2	2.6
Original + sebum + 10% linoleic (aged)	13.6	11.5	3.5

	Synthetic Sebum Wt.%	
	Regular	Modified
Palmitic acid	10.0	......
Stearic acid	5.0	......
Linoleic acid	5.0	20.0
Oleic acid	10.0	10.0
Cholesterol	5.0	5.0
Spermaceti	15.0	15.0
Coconut oil	15.0	15.0
Olive oil	20.0	20.0
Squalene	5.0	5.0
Paraffin	10.0	10.0

TABLE III
Effect of Emulsion Concentration of Modified Synthetic Sebum on Yellowness

	"b"		
	Cellulose	Polyamide	Polyester
Original	2.0	4.4	3.0
Aged original (no soil)	3.1	8.3	4.5
5% sebum emulsion	9.0	18.3	6.8
10% sebum emulsion	13.0	20.3	7.1
15% sebum emulsion	17.0	23.2	8.3
20% sebum emulsion	20.2	25.3	9.8

(10) which can increase yellowing and since soap is also formed during the washing process because of the fatty acids in the sebum, the presence of a small amount of amine soap may add to the reality of the soil rather than detract.

3) Based on the results in Part 2, a modified synthetic sebum emulsion was made so that yellowing could be developed in a minimum of time. The emulsion is made by adding 4 g of oleic acid and 8 g of triethanolamine to 100 g of the melted sebum. The modified sebum eliminated the need for multiple washes which are usually performed with the regular formula. Representative swatches were soiled in emulsions of varying concentrations (5%, 10%, 15%, 20%) and aged in the clothes dryer for one hour at a mean temperature of 217F (Table III).

Table III shows that the yellowing curve for cotton and Nylon are almost linear with concentration. In addition, they are almost parallel from 10% to 20%. Again, Dacron shows little yellowing at any concentration under these conditions.

4) By setting the regulator of the clothes dryer at three different positions, data were collected regarding the effect of temperature on yellowing. A 10% aqueous emulsion of the modified sebum was applied to the same fabrics used previously. These soiled fabrics were aged for one hour at each of the respective temperatures. By subtracting the aged original from the aged soiled fabric, the yellowing caused by sebum alone can be calculated (Fig. 3). Loeb (16) used the scorch test to show the heat yellowing of cotton fabric and plotted the log of time against the reciprocal of temperature as expressed in Rankine degrees. The relationship was linear. He concluded that the regression equations which represented oily cotton indicated that the yellowing was a result of mechanisms different from the other systems studied.

5) The experimental data that have been presented so far deal with the yellowing effects of sebum on unwashed material. The literature (6–10) is in agreement that ordinary washing of soiled fabric leaves a sebum residual of from 30–60%, depending on the substrate, temperature, builders, etc. It is logical to assume that a rapid aging of the residual sebum, after washing under various conditions, should give "yellow proof" of the efficiency of the active ingredients, builders, brighteners, etc., which are involved in the cleaning operation. The yellowness may be measured as a separate entity or as an expression representing whiteness, but in either case the final result should correlate with consumer use. The data from extraction procedures or radiotracer methods need not necessarily correlate because they are most often expressed as a weight percentage removal and do not of necessity represent color changes because of the removal of ingredients which develop color bodies.

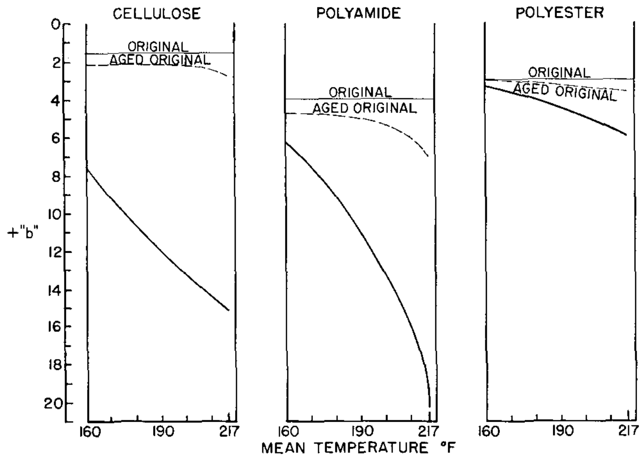

FIG. 3. Effect of temperature on yellowing. Conditions: soiling—modified sebum (20% linoleic); aging—clothes dryer, one hour.

A first step was to wash fabric soiled with the modified sebum in four detergent concentrations. The formula was a typical heavy-duty powder with 20% LAS, 35% TPP, 7% silicate, QS moisture, and sulfate. The test was run at 0.00, 0.05, 0.15, 0.25% concentrations. Swatches without soil were wetted and aged with the washed swatches so that the effect of aging on the fabric alone could be discounted.

Interpretation of the data in Table IV would lead to the conclusion that cellulose is cleaned much better at low concentrations than the synthetics. Polyamide improves most between 0.05 and 0.15% and shows no sebum removal at the lower concentration. Polyester makes the big jump at the high concentration. This information should be important in designing compositions, especially for cleaning the synthetics. It confirms the work reported by Hunter et al. (22). Fig. 4 combines the lightness values with the yellowness values and illustrates the change in whiteness (18) by using the formula L-3b (aged blank added).

6) The precision of the method was tested by calculating the mean and the variance for each set of swatches used in determining the effect of hardness on yellowing (23). Cotton swatches (20 in each bucket)

TABLE IV
Effect of Detergent Concentration on Developed Yellowness

	Original		Aged original		Percentage of concentration							
					0.00		0.05		0.15		0.25	
Fabric	L	b	L	b	L	b	L	b	L	b	L	b
Cellulose	93.5	+2.1	93.1	+3.0	89.2	+12.4	91.1	+10.2	91.8	+ 8.1	92.1	+ 6.4
Polyamide	92.2	+5.8	90.5	+8.9	79.4	+20.0	82.8	+21.1	88.8	+16.2	90.9	+12.1
Polyester	93.3	+2.6	90.1	+3.5	84.0	+13.2	27.7	+12.9	88.5	+10.9	91.1	+ 4.7

	"b" Units from Aged Original at Each Concentration				"b" Units Differences Between Concentrations		
	0.00	0.05	0.15	0.25	0.00–0.05	0.05–0.15	0.15–0.25
Cellulose	9.4	7.2	5.1	3.4	2.2	2.1	1.7
Polyamide	11.1	12.2	7.3	3.2	−1.1	4.9	4.1
Polyester	9.7	9.4	7.4	1.2	0.3	2.0	6.2

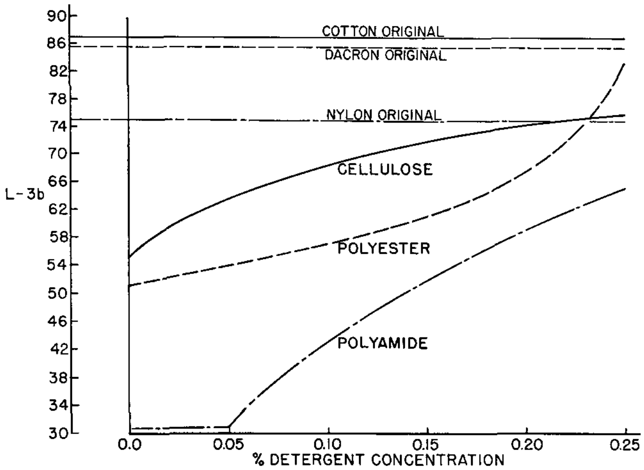

FIG. 4. Effect of detergent concentration on whiteness (L-3b). Conditions: soiling—modified sebum (20% linoleic); aging—clothes dryer, one hour at 217F; washing, 120F, 150 ppm hardness; formula—20% LAS, 7% silicate, 35% TPP, 8% water, Q. S. sulfate.

were washed in a typical heavy-duty composition at 0.15% detergent concentration at 120F and three different hardnesses. The hardness had a calcium-to-magnesium ratio of 3:2 and was expressed in terms of calcium carbonate. After washing, the swatches were aged for one hour in the clothes dryer at 217F. The confidence limit was calculated to be ± 0.4 "b" value at the 95% level.

7) Optical brighteners are used to counteract yellowness. The percentage used in some present-day detergent compositions is 0.5% or more. This means that the cost of this adjuvant is a significant portion of the cost of a heavy-duty detergent. The testing of the efficiency of optical brighteners has assumed greater importance (24). In many cases the brighteners are screened solely on unsoiled cloth. This eliminates

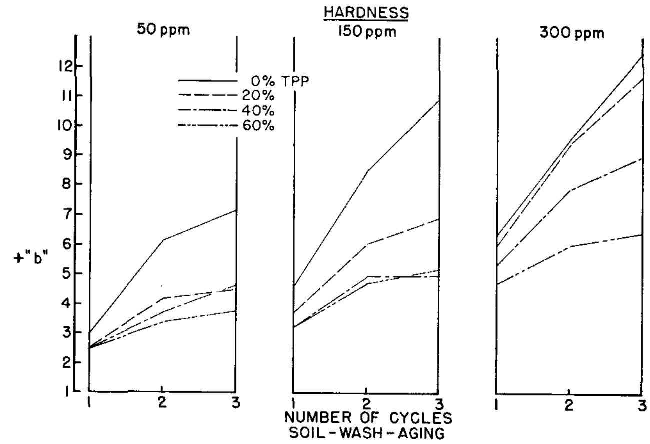

FIG. 6. Effect of TPP on yellowness. Conditions: soiling, regular sebum; aging, print dryer; washing, 0.15% detergent concentration, 120F; formula—20% LAS, 7% silicate, 8% water, Q. S. sulfate.

the reduction of ultraviolet intensity because of oil absorption and the reduction of brightener efficiency as a result of yellowing from residual sebum. The exhaustion can also be influenced by the presence of soil.

Four commercial heavy-duty detergent powders were tested to show the effect of heat and developed yellowing on brightening action. The products were simply chosen at random from the grocer's shelf and will not be identified. The three fabrics were washed in the products as usual. In the second part of the test, additional swatches were washed in the products and aged. In the last part of the test, a third set of swatches was soiled with the modified sebum, then washed in the respective products and aged (Table V).

Fig. 5 shows the relationship of the final "b" values. A chart could be drawn to show the total chromaticity

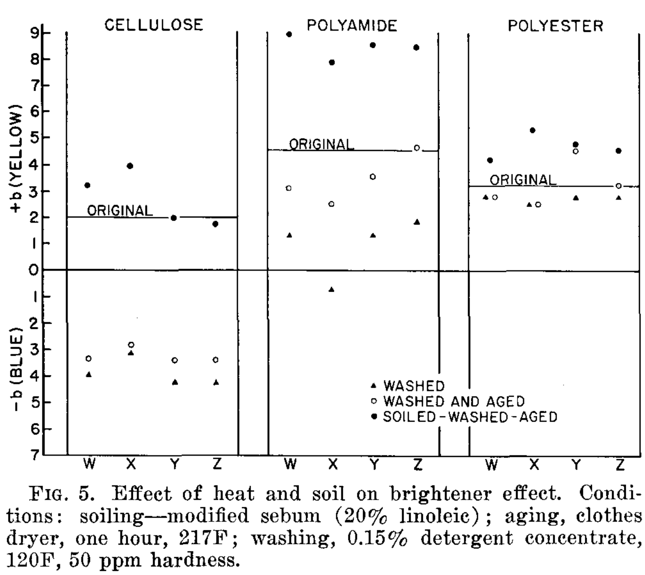

FIG. 5. Effect of heat and soil on brightener effect. Conditions: soiling—modified sebum (20% linoleic); aging, clothes dryer, one hour, 217F; washing, 0.15% detergent concentrate, 120F, 50 ppm hardness.

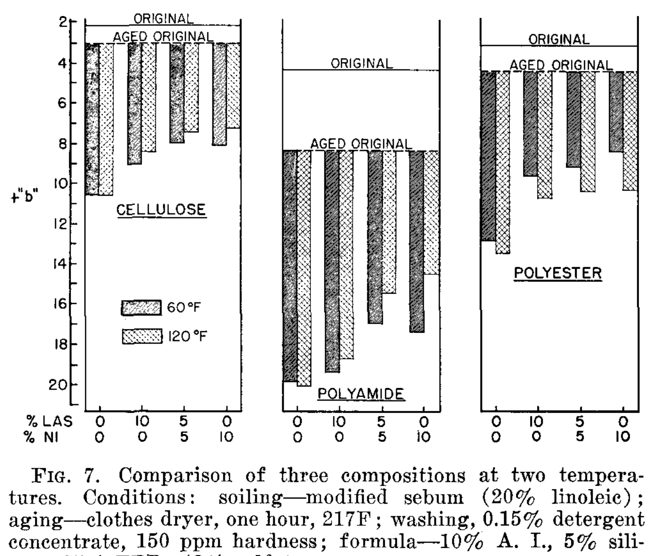

FIG. 7. Comparison of three compositions at two temperatures. Conditions: soiling—modified sebum (20% linoleic); aging—clothes dryer, one hour, 217F; washing, 0.15% detergent concentrate, 150 ppm hardness; formula—10% A. I., 5% silicate, 35% TPP; 42% sulfate.

TABLE V
Effect of Soil and Heat on Brightener Effectiveness
"a" and "b" Values

	No soil Washed No aging			No soil Washed Aged, 217F, 1 hr			Soil Washed Aged, 217F, 1 hr		
Product	C	N	D	C	N	D	C	N	D
W	+1.9 − 3.9	−0.2 + 1.3	−1.3 + 2.8	+1.8 − 3.4	−0.8 + 3.1	−1.3 + 2.8	0.0 + 3.2	−1.9 + 9.0	−1.5 + 4.2
X	+1.5 − 3.2	+0.9 − 0.8	−1.2 + 2.5	+1.5 − 2.9	−0.3 + 2.4	−1.2 + 2.4	−0.2 + 3.9	−1.7 + 7.9	−1.6 + 5.3
Y	+2.0 − 4.3	−0.2 + 1.3	−1.3 + 2.8	+1.7 − 3.4	−0.8 + 3.5	−1.3 + 4.6	−0.2 + 2.0	−2.0 + 8.6	−1.7 + 4.8
Z	+2.0 − 4.3	−0.5 + 1.9	−1.3 + 2.8	+1.7 − 3.4	−1.4 + 4.6	−1.4 + 3.2	+0.3 + 1.8	−2.1 + 8.5	−1.7 + 4.6

TABLE VI
Effect of Detergent Composition-Temperature on Yellowness
"b"
Reduction in Yellowness

60F									120F								
Cellulose			Polyamide			Polyester			Cellulose			Polyamide			Polyester		
LAS	50/50	NI	LAS	50/50	NI	LAS	50/50	NI	LAS	50/50	NI	LAS	50/50	NI	LAS	50/50	NI
1.5	2.6	2.6	0.5	2.9	2.5	3.2	3.7	4.5	2.1	3.1	3.4	1.3	4.7	5.5	2.7	3.2	3.3

effect. However, omitting the red-green data, it may be seen that on cotton the brighteners in W and X are not affected by heat as much as Y and Z, but they are less effective under soiled conditions than Y and Z. The results on synthetics are somewhat unreal because present-day fabrics have brighteners incorporated during the manufacturing process. Nevertheless, in the case of Nylon, product X is the best, notwithstanding its deterioration with heat. This same product is the poorest with soiled Dacron. As usual, there is not much brightening action with Dacron.

8) In the early stages of this work a study was made of the effect of TPP on reducing yellowness under different hardness conditions. The experiment was done in duplicate by using the regular sebum formula and aging after each wash. The swatches were enclosed in aluminum foil and dried in the Pako print dryer. Fig. 6 shows the result of this testing. The product used was a spray-dried detergent composition, using linear alkyl benzene sulfonate as the active ingredient. In a test of this type, detergent, hardness, temperature, metallic contaminants, bleach, fabric, etc., will influence the sequestering capacity. Therefore it is safe to assume that it will correlate more with practical laundering than the usual titration procedure or particulate removal.

9) A final experiment, attempting to show the utility value of the yellowing procedure, was made by comparing three detergent compositions at two temperatures. The compositions were mixtures of nonionics and anionics. The main purpose was to demonstrate that the mechanism of soil removal is dependent on fabric types and soil forms. The data presented may not be a final answer to the present-day developments but should serve as a stimulus to evaluate laundering procedures more realistically in a future era.

An analysis of Table VI and Fig. 7 shows the improvement in detergency attributable to the addition of a nonionic detergent. The greatest benefit on cellulose and polyamide is at the high temperature. This condition is reversed with polyester, where detergency is better at the low temperature.

The results and conclusions can be varied by the type of nonionic or anionic. Likewise, finishes and combinations of fibers can alter the situation. Nevertheless it is believed that the tool described can conplement present-day procedures in arriving at a true comparison.

ACKNOWLEDGMENT

Assistance in redesigning equipment provided by the Colgate-Palmolive Technical Engineering Department. Graphic illustrations provided by J. Russett.

REFERENCES

1. Spangler, W. G., JAOCS *41,* 300 (1964).
2. Spangler, W. G., H. D. Cross III, and B. R. Schaafsma, Ibid. *42,* 723 (1965).
3. Utermohlen, W. P., et al., Textile Res. J. 489 (1949).
4. Howarth, E., —. Piper, and H. R. Billica, Ibid. *36,* 857 (1966).
5. Wagg, R. E., and C. J. Britt, J. Text. Inst. Trans. *53,* T 205 (1962).
6. Scott, B. A., J. Appl. Chem., *13,* 133 (1963).
7. Gordon, B. E., et al., JAOCS *44,* 289 (1967).
8. Gilderson, R. W., paper presented at 53rd Annual Meeting, CSMA, Hollywood, Fla., December, 1966.
9. Powe, W. C., JAOCS *40,* 290 (1963).
10. Oldenroth, O., Fette Seifen Anstrichmittel, *61,* 1142 (1959).
11. Huggins, J. M., Monsanto Company, private communication.
12. Clayton, G., Union Carbide Company, private communication.
13. McLendon, V., and F. Richardson, Am. Dyestuff Reptr. *52,* 27 (1963).
14. McLendon, V., and F. Richardson, Ibid. *54,* 15 (1965).
15. Wagg, R. E., et al., 4th Int. Congress Surface-Active Agents, 1964.
16. Loeb, L., et al. Am. Dyestuff Reptr. *55,* 703 (1966).
17. Privett, O. S., M. L. Blank, J. B. Covell and W. O. Lundberg, JAOCS *38,* 22 (1961).
18. Walker, K., and L. J. Williamson, Bulletin 968, June 1961, Cornell Univ. Agr. Exp. Station, Ithaca, N.Y.
19. Franks, F., and B. J. Roberts, J. Appl. Chem. *15,* 109 (1965).
20. O'Neill, L. A., et al., Chem. and Ind. 1796 (1962).
21. Rochas, P., and J. C. Martin, Bull. Inst. Text. France *83,* 41 (1959).
22. Hunter, R. T., H. L. Marder, and C. R. Kurgan, JAOCS Fall Meeting, Philadelphia 1966.
23. Schwartz, A. M., and J. Berch, Soap and Chem. Spec. *39,* 78 (1963).
24. Stensby, P. S., Detergent Age *3,* 20 (1967).

[Received May 26, 1967]