

glycerides should differ in any fundamental manner in plants and in animals. On the contrary, it is maintained that the characteristic glyceride structure of stearic-rich animal body fats can be more satisfactorily accounted for by the alternative explanation which has been discussed in this communication and which has been accepted by the writer and his co-workers for some considerable time.

### Summary

Comparative study of the constituent glycerides of a number of ox, sheep, and pig body fats which have been investigated in the Liverpool laboratories reveals that, while there is considerable accordance between the values observed for the trisaturated and monounsaturated groups of glycerides with those calculated from probability considerations, there is complete divergence between the latter and the values observed for the di- and triunsaturated glycerides.

The views on animal body fat glyceride structure developed and maintained by Hilditch and co-workers are shown to be in harmony with the arithmetical relationships referred to (Table I), while they do not require the postulate that enzyme synthesis of glycerides should differ fundamentally in animal and in vegetable cells.

It is shown that apparent resemblance in the proportions of the four categories of saturated and unsaturated glycerides to those calculated on probability considerations may arise in a number of different ways, and that such resemblance has not necessarily any bearing on the mode of glyceride structure observed in fats.

The well-established fact that mixed glycerides produced at high temperatures by synthesis or by

acyl interchange approximate to "random" (probability) distribution also has no bearing upon the matter of the structure of mixed glycerides produced by the synthetic action of enzymes at or near atmospheric temperatures in the living cell.

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## Report of the Oil Color Committee—1948

AT the Color Committee meeting held in New Orleans at the time of the Spring A.O.C.S. Convention it was the unanimous decision of the members to investigate during the coming year the reproducibility of the Coleman Jr. spectrophotometers and to attempt to determine just what readings would be most advantageous if a spectrophotometric method for color grading was set up. In order to accomplish this purpose 12 oils were submitted to 25 collaborators, each of whom was asked to read spectrophotometric transmissions in "B" type 25-mm. cuvettes at specified wavelengths, to read the Lovibond color, and to assign an arbitrary eye grade to the oils, assuming the lightest oil to have a grade of one and the darkest 25. Each collaborator was also asked to prepare and read the spectrophotometric curve on a solution of nickel sulfate prepared by dissolving 20.000 grams of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in water and diluted to a total volume of 100 ml.

### Work Done

Twenty laboratories reported data on the oils submitted for examination. The complete spectral characteristics of the 12 oils are shown in Figures 1, 2, and 3. Eleven laboratories reported results on the nickel sulfate solution using the Coleman Jr. spec-

trophotometer while three laboratories reported using the Beckman spectrophotometer. The Beckman results are calculated to the measured diameter of the cuvettes used in the Coleman results. Figure 4 shows the composite data obtained on the Coleman Jr. and Beckman instruments for the nickel sulfate solution.

### Discussion of Data

In discussing the data reported, it seems logical to divide the material into two parts, the first part dealing with the results obtained on the oil samples and the second part dealing with the results obtained on the nickel sulfate solution.

### Data on Oil Samples

The composite data or the average data for all of the laboratories of the 12 oils which were submitted for transmission and other measurements is shown in Table I. One of the primary objectives of this work was to attempt to correlate density measurements at 550  $\mu\mu$ , Lovibond colors, color index at more than one wavelength, and such other measurements as might seem desirable with eye gradings. At the bottom of Table I are shown the essential figures necessary for these correlations.

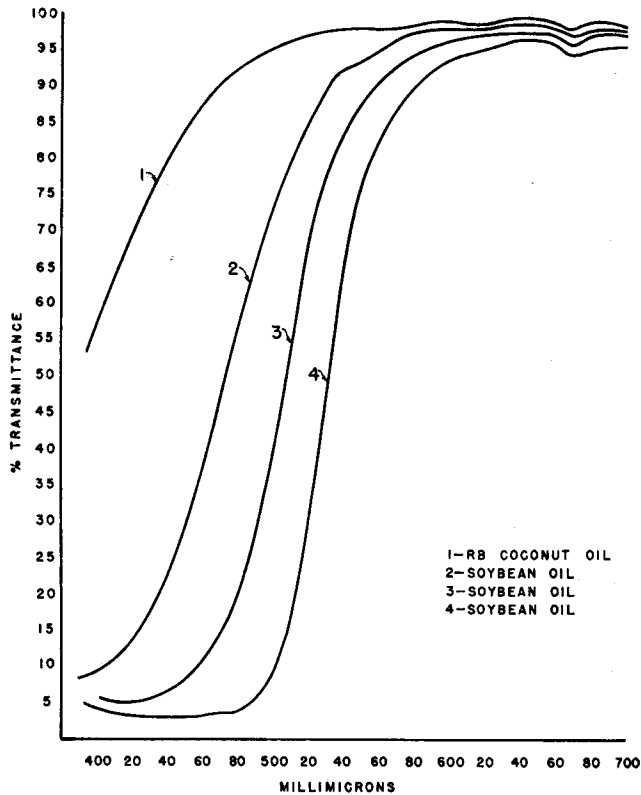


Fig. 1. A.O.C.S. oil transmissions.

Using the Spearman-Brown rank order correlation equation,

$$r = 1 - \frac{6\sum d^2}{N(N^2 - 1)}$$

The calculated coefficients are:

Density at 550  $m\mu$ . vs. eye grade = 0.951  
 Color index vs. eye grade = 0.944  
 Lovibond red vs. eye grade = 0.986.

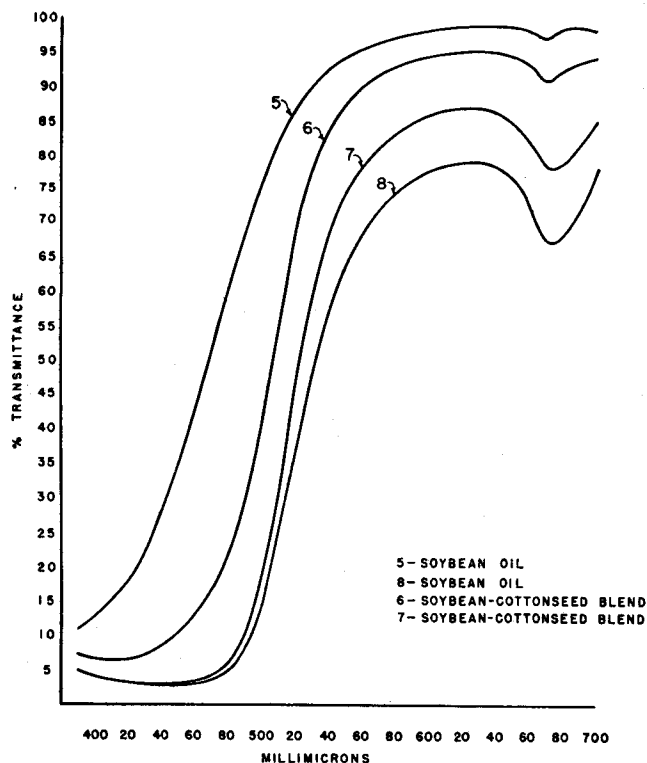


Fig. 2. A.O.C.S. oil transmissions.

These correlations are all of such a high order that, considering the number of samples involved, there is little to choose between various methods of grading the oils if the eye grade is considered to be the essential criterion.

In order to establish more fully the relationship between eye grading and density measurements at 550  $m\mu$ . and Lovibond red readings, which are essentially density values, the average of the eye grades were plotted against actually determined Lovibond colors on the one hand and Lovibond red values calculated by the equation:

$$\text{Lovibond red} = \frac{\text{Density at } 550 \text{ } m\mu. \times 100}{1.3}$$

The relationship between red readings and eye gradings was found to be logarithmic which is to be expected from the Weber-Fechner law, which states that the increment of color divided by the actual color is equal to a constant, or in other words, that the number of perceptible differences in terms of Lovi-

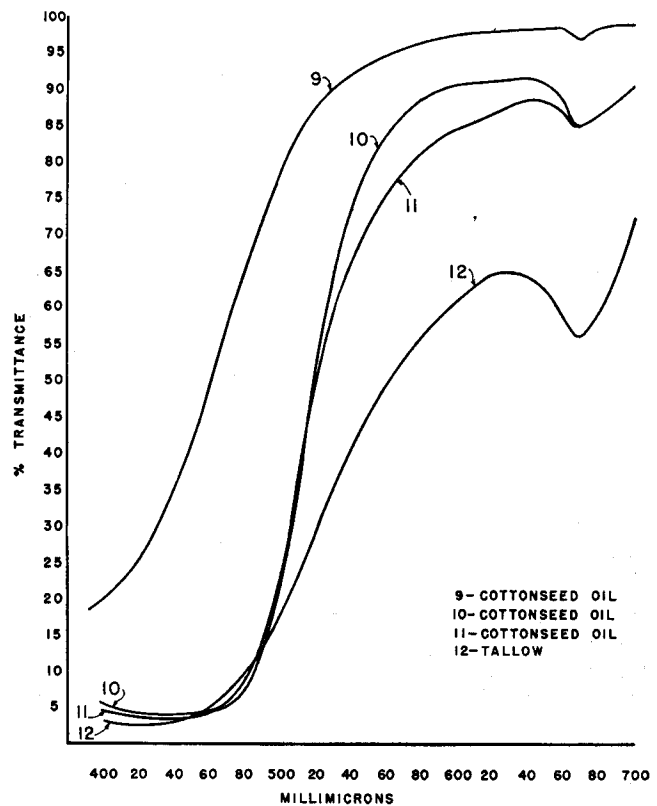


Fig. 3. A.O.C.S. oil transmissions.

bond red increases as the color of the oil decreases. In Figure 5 eye grade is plotted against Lovibond red on a semi-log paper. A straight line results. The calculated values actually fall closer to the line than do the measured Lovibond red colors. As a result of these findings, it can be concluded that the density measurement at 550  $m\mu$ . is certainly as good, if not better, than Lovibond red in predicting the positioning by eye of oil colors.

The reproducibility of data between laboratories is best illustrated by means of the curve shown in Figure 6. The data plotted in this curve are taken both from the results on the 12 oil samples and on the

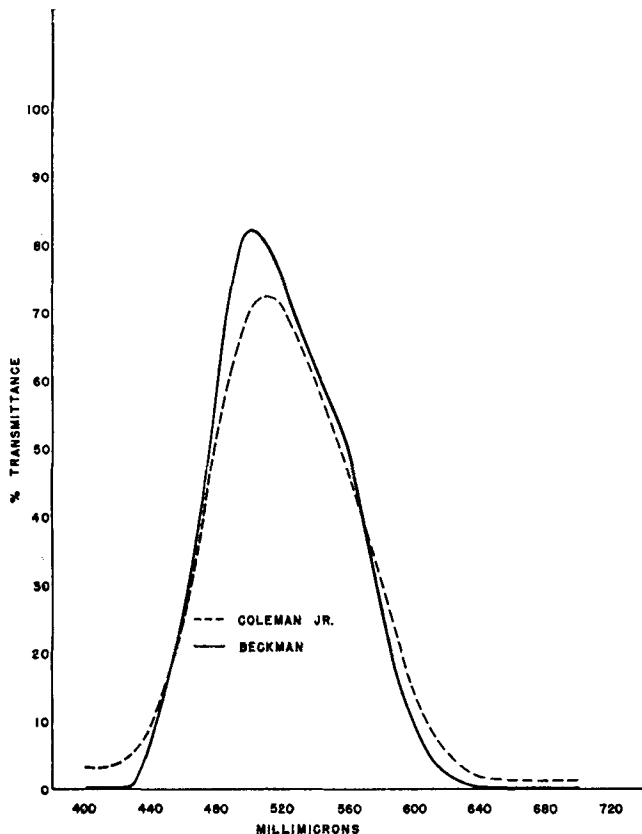


Fig. 4. Nickel sulfate solution.

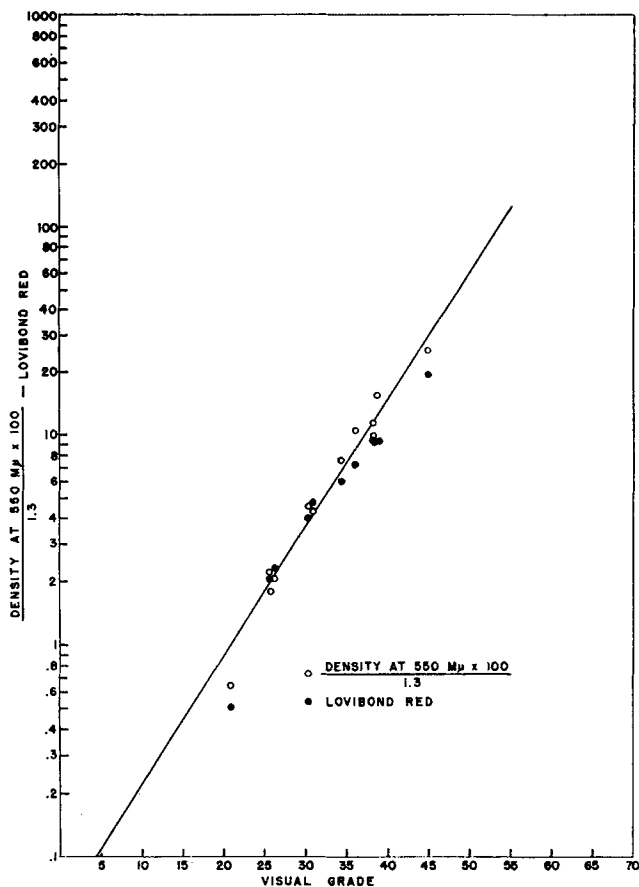


Fig. 5. Visual grade vs.

$$\frac{\text{Density at } 550 \text{ m}\mu \times 100}{1.3} \text{ and Lovibond red color.}$$

nickel sulfate solution. It is interesting to note that the standard deviation is about 0.4% transmittance at 0 and 100% transmittance levels and increases as the transmittance goes toward the 50% level to about 2.0% transmittance. The 0 and 100% transmittance points are the calibration points of the instrument.

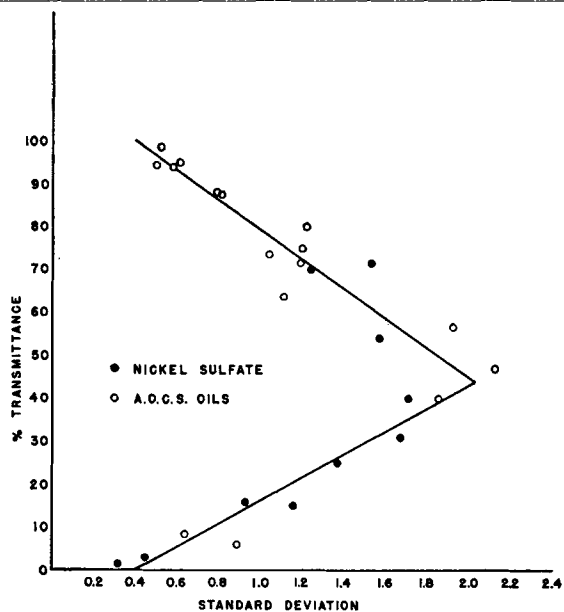


Fig. 6. Reproducibility of readings.

They are also the points of least sensitivity. Both of these factors may contribute to the decreased reproducibility as the readings move toward the 50% transmittance point. In order to compare the degree of reproducibility of results obtained on the Coleman instrument with Lovibond red values on the oil samples the standard deviation or sigma was calculated for each of the oils at 550 mμ. Sigma was also calculated for the Lovibond red readings. The sigma at 550 mμ was calculated to an equivalent Lovibond red value. In Table II is shown the mean value of the

TABLE II  
Calculation of Variance in Oil Readings

Oil No.	Mean Value 550 mμ.	Sigma 550 mμ.	Mean Lov. Red	Sigma Lov. Red	Sigma 550 mμ. Calc. to Lov. Red Units
1.....	98.22	0.525	0.51	0.15	0.18
2.....	94.33	0.509	2.31	0.24	0.18
3.....	88.08	0.790	4.82	0.31	0.30
4.....	74.77	1.205	9.30	0.59	0.52
5.....	94.98	0.614	2.03	0.22	0.22
6.....	87.50	0.816	4.04	0.31	0.31
7.....	73.39	1.042	7.21	0.42	0.47
8.....	63.65	1.111	9.22	0.53	0.59
9.....	93.91	0.586	2.10	0.25	0.21
10.....	80.01	1.223	5.98	0.38	0.51
11.....	71.47	1.195	9.18	0.49	0.55
12.....	46.75	2.124	19.67	3.30	1.52

transmittance for the 12 oils at 550 mμ., the calculated sigma at 550 mμ., the mean Lovibond red color, the sigma of the Lovibond red values, and sigma at 550 mμ. calculated to Lovibond red units. The obvious conclusion from these data is that using a large number of spectrophotometers operated by an equally large number of different operators almost exactly the same precision is obtained by both methods at low Lovibond red levels and that greater precision is obtained by using the spectrophotometer at high Lovibond red levels.

TABLE I  
 Composite Data on Oil Samples

	1	2	3	4	5	6	7	8	9	10	11	12
Lovibond Yellow.....	3.61	23.78	33.98	38.70	21.91	35.96	46.40	58.01	20.83	38.00	43.76	95.00
Lovibond Red.....	0.51	2.31	4.82	9.30	2.03	4.04	7.21	9.22	2.10	5.98	9.18	19.67
Eye Grade.....	1.0	6.38	11.08	18.57	5.91	10.47	16.06	18.96	5.87	14.63	18.30	25.00
Transmission												
400 m $\mu$ .....	57.30	11.04	6.10	4.68	13.06	7.30	4.82	4.21	20.95	5.78	4.62	3.53
450 m $\mu$ .....	84.08	32.04	8.35	3.41	37.56	10.24	3.57	3.13	43.28	4.16	3.90	4.35
500 m $\mu$ .....	95.16	74.18	39.91	9.64	77.31	40.87	17.98	13.98	78.80	22.06	21.92	20.59
550 m $\mu$ .....	98.22	94.33	88.08	74.77	94.98	87.50	73.39	63.65	93.91	80.01	71.47	46.75
600 m $\mu$ .....	99.05	98.17	96.36	93.86	98.32	94.40	85.90	77.72	97.61	90.68	84.94	62.35
620 m $\mu$ .....	99.16	98.62	97.27	95.66	98.75	95.15	86.74	79.17	98.04	91.40	87.32	66.08
640 m $\mu$ .....	99.22	98.67	97.41	96.30	98.85	95.07	86.61	78.61	98.13	91.35	88.57	66.09
650 m $\mu$ .....	99.20	98.62	97.33	96.10	98.86	94.19	84.60	75.71	98.13	90.18	88.11	63.51
660 m $\mu$ .....	99.25	98.60	97.25	95.75	98.93	93.32	81.63	71.31	97.89	88.05	86.70	60.37
670 m $\mu$ .....	99.15	98.34	97.16	95.12	98.76	92.18	78.92	67.50	97.79	86.21	85.70	59.07
680 m $\mu$ .....	99.11	98.52	97.30	95.09	98.72	91.93	78.69	67.13	97.87	85.80	85.74	60.98
700 m $\mu$ .....	98.54	98.05	97.18	95.56	98.08	93.95	85.76	78.08	97.76	90.44	89.78	74.08
Den. at 550 m $\mu$ .....	0.077	.0254	.0550	.1263	.0223	.0580	.1344	.1962	.0273	.0969	.1468	.3300
D X 100 $\div$ 1.3.....	0.59	1.95	4.23	9.72	1.72	4.46	10.34	15.10	2.10	7.45	11.30	25.40
Den. Order.....	1	3	5	8	2	6	9	11	4	7	10	12
Eye Order.....	1	4	6	10	3	5	8	11	2	7	9	12
Lovibond Order.....	1	4	6	11	2	5	8	10	3	7	9	12
Color Index (450, 550, 670).....	281.45	224.71	193.59	173.30	231.30	189.92	155.88	134.28	234.98	170.38	161.07	110.17
Color Index Order.....	1	4	5	7	3	6	10	11	2	8	9	12

In the original instructions each collaborator was asked to read the oil transmissions in a "B" type 25-mm. cuvette and to report the inside dimensions of the cuvette or the average if more than one cuvette was used. Actual values reported indicate that the dimensions of the cuvettes varied from 21.2 mm. to 22.0 mm. This difference is as great as the difference between the internal measurement of type A and type C cuvettes. Ten type A, B, and C cuvettes were measured and found to have average internal diameters of 21.3, 21.84, and 22.13 mm. respectively. The transmittance values obtained, using a refined and bleached cottonseed oil in A, B, and C cuvettes, are shown in Table III. The maximum spread between

submitted for examination by the Committee. The 12 oil samples were read in these three instruments and in a regular instrument purchased from a supply house (Instrument A-1532). The manufacturer's specification on the other three instruments were as follows:

## Instrument A-1795

Band width, lower limit  
 Stray light at 400, just over mean  
 Calibration at 440  $\pm$  1.5 m $\mu$ . at limits  
 at 610 - 0.6 m $\mu$ . at limits.  
 Ref. CH 87.

## Instrument A-1693

Band width one-fourth way from lower towards upper limit  
 Stray light at 400, less than mean  
 Calibration at 440 - 1.5 m $\mu$ . at limits  
 at 610 + 0.6 m $\mu$ . at limits.  
 Ref. CH 88.

## Instrument A-2084

Band width just over upper limit  
 Stray light at 400, upper limit  
 Calibration at 440, at mean  $\pm$  0 m $\mu$ .  
 at 610, at mean  $\pm$  0 m $\mu$ .  
 Ref. CH 88.

The data obtained with the four instruments are shown in Table IV. In general, the results indicate that machines held within the manufacturer's tolerances give reasonably reproducible results in the hands of a single operator. In these tests the same standardizing filter was used for all of the machines, eliminating that variable in the readings.

## Data on Nickel Sulfate

After a number of tests employing nickel sulfate, copper sulfate, and ferric chloride it was found that a straight nickel sulfate solution gave the most promise of being a suitable solution for checking the Coleman Jr. spectrophotometers for band width, wavelength adjustment, stray light, and response at any transmittance level. The nickel sulfate solution containing 20 grams of NiSO<sub>4</sub>·6H<sub>2</sub>O in 100 ml. of solution was selected as the best solution to use since this gave approximately 50% transmittance at 550 m $\mu$ ., a reasonably sharp peak at 510 m $\mu$ ., and, as measured by the Beckman instrument, no transmission below 420 m $\mu$ . or above 640 m $\mu$ . The Beckman and Coleman results are plotted in Figure 4.

It has already been pointed out that the standard deviation on nickel sulfate obtained by the various

 TABLE III  
 Checking A, B, and C Cuvettes  
 Refined and Bleached Cottonseed Oil

25 mm. Round Type C										22.13 mm. Average		
400	20.3	20.3	20.3	20.3	20.3	20.3	20.0	20.2	20.4	20.5		
450	44.6	44.3	44.1	44.1	44.1	44.0	43.9	44.1	44.5	44.6		
500	80.2	79.9	79.6	80.3	80.0	80.1	80.0	80.0	80.0	80.3		
550	93.8	93.9	94.0	94.5	94.2	94.0	94.3	93.9	94.5	94.2		
600	97.4	97.4	97.0	97.4	96.9	97.4	96.8	96.3	96.9	96.7		
650	97.5	97.7	97.7	97.6	97.7	97.5	97.4	97.7	98.2	97.7		
700	97.2	97.7	97.8	98.0	97.7	97.5	97.9	97.5	97.6	97.7		
25 mm. Round Type B										21.84 mm. Average		
400	21.2	21.3	21.4	21.5	21.4	21.7	21.7	22.3	22.4	21.8		
450	45.2	45.4	45.5	45.3	45.1	45.4	45.4	45.9	46.1	45.6		
500	79.5	79.3	79.4	79.5	79.3	79.0	79.2	79.5	79.6	79.6		
550	94.0	93.9	94.3	93.9	93.5	93.0	93.2	93.7	93.9	93.3		
600	98.0	97.7	97.8	97.7	97.7	97.3	97.4	97.5	97.7	97.7		
650	98.2	98.0	98.0	97.7	97.9	97.5	97.4	97.6	97.6	97.5		
700	97.3	97.2	97.4	97.0	97.2	96.8	97.2	97.2	97.3	97.4		
25 mm. Round Type A										21.3 mm. Average		
400	22.0	22.0	22.6	22.7	22.7	22.8	23.2	23.2	22.9	23.3		
450	45.2	44.9	45.6	45.9	45.5	45.7	46.3	46.2	45.9	46.5		
500	79.9	79.1	79.8	80.0	79.8	79.9	79.9	79.9	80.0	80.3		
550	94.0	93.3	93.7	93.9	93.9	93.8	93.5	93.8	93.3	93.5		
600	97.6	96.9	97.6	97.6	97.3	97.8	97.3	97.8	97.5	97.5		
650	97.6	97.7	97.9	97.9	97.6	97.6	97.5	97.5	97.5	97.5		
700	97.5	97.9	97.7	98.0	97.7	97.9	97.8	98.1	97.7	98.0		
Average	A	B	C									
400	22.74	21.67	20.29									
450	45.77	45.49	44.23									
500	79.86	79.39	80.03									
550	93.67	93.67	94.13									
600	97.49	97.65	96.95									
650	97.63	97.72	97.67									
700	97.83	97.20	97.64									

readings is approximately 2½%. However, differences are by no means uniform, indicating that errors, other than those that occur in the cuvettes, overshadow even the difference between A cuvettes and C cuvettes.

Three instruments representing the production limits for the Coleman Jr. spectrophotometers were

TABLE IV  
 25 mm. "B" Cavettes, CCl<sub>4</sub> Standard

Wavelength in mμ.	Sample No. 1				Sample No. 2				Sample No. 3			
	Instrument No.				Instrument No.				Instrument No.			
	A 1532	A 1795	A 1693	A 2084	A 1532	A 1795	A 1693	A 2084	A 1532	A 1795	A 1693	A 2084
400.....	56.7	58.1	56.5	58.8	10.2	12.0	10.5	12.8	5.7	7.0	6.0	8.0
420.....	69.2	71.5	69.3	70.0	14.2	16.0	14.0	16.2	5.1	6.3	5.0	6.8
440.....	80.0	81.0	80.0	80.0	24.0	25.5	23.5	25.7	6.3	7.5	6.3	8.2
450.....	85.8	86.5	85.2	85.5	32.0	33.5	30.7	33.5	8.0	9.5	7.9	10.0
460.....	87.5	88.4	87.5	86.5	39.8	40.5	38.5	39.5	10.9	11.8	10.5	12.0
480.....	93.0	92.8	92.8	92.0	58.6	58.0	57.9	58.0	21.0	21.2	20.0	22.9
500.....	96.0	96.2	96.3	95.5	74.5	74.6	74.5	73.9	40.6	41.0	40.0	42.2
520.....	97.8	97.3	97.9	97.5	85.9	85.8	86.5	85.0	66.0	66.2	65.5	65.8
540.....	98.3	97.8	98.6	96.8	92.2	91.3	92.5	90.9	83.5	82.8	83.5	81.5
550.....	98.6	98.7	98.9	98.5	94.2	94.0	94.7	94.0	88.6	87.5	88.3	88.0
560.....	99.0	98.5	99.2	99.0	96.0	95.3	95.7	95.5	92.0	91.2	91.5	90.5
580.....	99.1	99.5	99.5	99.3	97.8	97.0	97.5	97.1	95.0	94.2	94.7	94.5
600.....	99.2	99.5	99.9	99.5	98.0	98.0	99.1	97.8	96.5	96.5	97.0	96.1
620.....	99.5	99.1	99.4	99.5	98.5	98.0	98.0	98.5	97.0	96.8	97.3	97.0
640.....	99.3	99.5	99.7	99.5	98.3	98.0	99.0	97.3	97.5	97.2	97.3	94.1
650.....	99.8	99.6	99.3	98.5	99.0	98.5	98.0	97.2	97.5	96.5	96.5	95.3
660.....	99.5	99.5	99.9	99.0	98.0	98.5	98.9	97.5	97.0	97.0	97.9	96.5
670.....	97.8	99.8	99.9	99.0	96.5	98.5	98.5	97.0	95.0	97.2	97.5	96.0
680.....	99.0	99.8	100.0	99.0	98.0	98.6	98.9	98.0	97.0	97.5	97.8	97.0
700.....	98.5	100.0	99.2	98.9	97.5	99.0	98.2	97.8	97.5	98.0	97.5	97.0
	Sample No. 4				Sample No. 5				Sample No. 6			
400.....	4.4	5.5	4.8	6.5	12.5	14.0	12.5	15.4	6.8	8.1	7.2	9.2
420.....	3.5	4.3	3.5	5.0	17.9	19.5	17.3	20.0	6.9	8.0	6.8	8.5
440.....	3.2	4.0	3.2	4.7	29.1	30.3	28.5	31.0	8.5	9.6	8.5	10.0
450.....	2.8	4.4	3.0	4.5	44.0	45.0	42.8	45.0	10.0	11.7	10.0	12.1
460.....	3.5	4.3	3.3	4.7	45.3	46.0	44.0	45.3	12.6	13.8	12.4	14.0
480.....	4.0	5.0	4.0	6.0	63.0	62.8	62.3	62.8	21.8	22.2	21.2	23.8
500.....	9.3	10.5	9.3	12.5	77.0	78.0	77.8	77.0	41.0	41.8	40.8	43.0
520.....	31.8	33.0	31.5	35.4	87.4	88.0	87.9	86.8	67.0	67.8	66.5	66.6
540.....	64.8	64.2	64.0	62.9	93.3	92.5	93.7	91.4	83.8	82.8	84.0	81.7
550.....	76.0	75.5	76.0	74.2	95.0	95.0	95.7	95.0	87.9	87.5	88.1	87.0
560.....	83.5	83.1	83.5	82.0	96.8	96.5	97.0	96.1	91.0	90.5	90.9	90.0
580.....	91.0	90.5	91.0	89.8	97.5	98.0	98.0	97.1	93.5	93.5	93.5	92.5
600.....	94.0	94.5	94.8	93.8	98.3	98.5	99.0	98.2	94.5	94.5	95.0	94.3
620.....	96.0	96.0	95.6	95.5	98.7	98.5	98.1	98.5	95.0	94.7	94.9	94.5
640.....	96.1	97.2	96.8	93.1	98.0	99.0	98.8	95.5	94.5	94.5	94.9	91.3
650.....	96.1	96.0	95.6	93.5	97.8	97.7	97.3	95.3	94.0	93.5	93.1	91.0
660.....	97.2	95.8	96.2	94.7	101.0	98.5	99.0	98.3	95.0	93.0	93.4	92.3
670.....	93.3	95.9	95.5	94.1	96.5	99.0	98.8	97.5	90.5	92.8	92.0	91.1
680.....	95.0	95.2	95.5	95.0	98.5	98.9	98.7	98.9	92.0	91.9	92.2	92.5
700.....	95.7	97.0	96.0	95.8	98.5	99.5	98.5	98.2	94.2	95.2	94.1	94.0
	Sample No. 7				Sample No. 8				Sample No. 9			
400.....	4.6	5.5	4.8	6.5	3.8	4.8	4.0	5.7	19.8	21.4	19.6	22.5
420.....	3.6	4.3	3.5	5.0	3.1	3.8	3.0	4.3	25.5	27.1	25.5	27.5
440.....	3.2	4.2	3.2	4.6	2.9	3.6	3.0	4.1	36.2	37.1	35.5	37.5
450.....	3.0	4.4	3.2	4.8	2.5	4.0	2.8	4.0	37.8	38.9	36.3	39.0
460.....	3.7	4.5	3.5	5.1	3.2	4.0	3.0	4.5	50.3	51.5	49.5	50.9
480.....	5.5	6.5	5.5	8.0	4.3	5.2	4.2	6.5	66.2	66.5	65.8	66.0
500.....	17.5	18.2	17.0	20.6	13.9	14.0	13.2	16.0	78.2	80.0	79.3	78.0
520.....	43.5	44.2	43.0	44.9	35.6	36.0	34.5	36.8	87.4	88.2	87.2	87.0
540.....	66.9	66.0	66.0	65.0	56.9	56.0	56.6	55.5	92.0	91.8	92.5	90.5
550.....	74.0	73.1	74.0	72.2	64.0	63.8	64.0	63.0	94.0	94.2	94.6	93.1
560.....	78.5	78.0	78.1	77.2	69.0	69.0	69.0	68.3	95.5	96.5	96.0	95.0
580.....	84.0	83.5	83.5	82.7	76.0	75.0	75.5	74.2	97.5	97.0	97.0	96.5
600.....	86.0	85.9	86.2	85.2	78.0	77.7	78.5	77.2	97.5	98.0	98.0	97.6
620.....	87.0	86.5	86.7	86.1	79.3	78.8	79.1	78.8	98.1	97.8	97.8	98.3
640.....	86.2	86.8	86.5	82.7	78.5	78.5	78.6	74.3	97.5	98.5	98.0	94.0
650.....	84.9	84.2	83.8	81.3	76.0	75.3	74.5	72.6	98.2	97.8	97.9	96.0
660.....	82.5	81.5	82.1	81.0	71.5	71.2	71.8	70.5	97.8	98.2	98.9	97.5
670.....	77.3	79.3	79.0	78.8	66.5	67.8	67.5	67.9	96.0	99.0	98.0	96.9
680.....	78.5	78.4	78.8	79.5	67.0	66.8	67.6	68.8	98.0	98.0	98.5	98.5
700.....	85.5	86.9	86.5	86.2	77.5	78.3	78.8	79.0	99.0	99.7	98.6	99.0
	Sample No. 10				Sample No. 11				Sample No. 12			
400.....	5.6	6.5	6.0	7.6	4.3	5.5	4.6	6.4	2.7	4.4	3.5	4.5
420.....	4.3	5.0	4.1	5.7	3.5	4.3	3.5	5.0	3.5	3.8	3.0	4.0
440.....	3.9	4.8	3.8	5.2	3.5	4.3	3.5	5.0	3.0	4.3	3.5	4.7
450.....	3.5	5.0	4.0	5.5	3.5	4.9	3.8	5.3	5.5	6.0	5.3	7.3
460.....	4.4	5.5	4.3	6.0	4.4	5.5	4.3	6.0	5.5	7.8	7.0	7.5
480.....	7.2	8.5	7.1	10.0	8.0	9.0	8.0	10.3	11.3	14.5	14.0	13.5
500.....	21.3	22.5	21.5	24.2	21.5	22.5	21.5	23.5	20.5	24.0	23.5	22.7
520.....	49.0	50.8	49.0	50.5	44.7	46.5	44.8	46.0	31.7	34.2	33.8	32.8
540.....	73.9	73.0	73.8	71.5	64.5	65.0	65.0	63.1	42.8	44.3	44.5	43.5
550.....	80.2	80.9	81.0	79.0	71.0	71.3	71.8	70.0	47.5	49.0	48.8	47.7
560.....	85.0	85.8	85.3	84.0	75.2	76.0	75.8	74.3	51.5	53.2	53.0	52.5
580.....	89.5	89.5	90.0	88.9	81.2	81.0	81.7	80.5	58.5	59.8	59.9	58.8
600.....	90.5	91.5	91.9	90.6	84.2	85.0	85.7	84.5	63.0	64.5	64.5	63.0
620.....	92.0	91.8	92.0	91.8	87.2	84.0	87.4	86.6	67.0	68.0	68.3	66.5
640.....	91.0	92.2	92.0	87.3	87.3	88.9	88.5	84.2	67.5	67.3	67.5	65.8
650.....	90.5	89.5	89.1	87.2	88.0	86.9	86.8	84.6	65.8	63.1	64.5	62.0
660.....	88.2	88.5	89.1	87.5	86.3	86.9	88.0	86.0	60.0	60.7	61.1	61.3
670.....	84.6	87.4	86.5	86.0	84.0	86.5	86.0	85.0	58.8	59.0	60.0	60.5
680.....	85.8	86.0	86.5	86.9	85.5	86.0	86.5	86.1	60.7	60.8	62.1	62.0
700.....	91.0	92.0	91.5	91.8	90.0	91.0	90.8	90.5	74.0	73.3	75.9	74.5

laboratories corresponds almost exactly to the deviation found for the oils. The standard deviation for the oils and the nickel sulfate solution is plotted in Figure 6. For each collaborator's results an order number has been assigned at each of the wavelengths at which the nickel sulfate was measured. If these order numbers are averages, it gives us a measure of the position of each of the laboratories with respect to the mean, which in this case would be 6 since 11 laboratories reported. The order number for the various collaborators is as follows:

Laboratory Number	Order Average
1	7.20
6	4.57
8	5.59
13	8.27
12	5.63
5	8.38
11	5.75
18	3.94
14	3.94
2	8.53
7	4.05

Laboratories 7, 14, and 18 are considerably below the average while 2, 5, and 13 are high; 7 and 14 are low throughout the entire range while 2, 5, and 13 are high. As far as these results are concerned, it can only be assumed that the nickel sulfate solution used differed somewhat from the average or that the instrument response was generally too high or too low. Laboratory 18 gave extremely low results in the range of maximum transmittance but tended to be high at low transmittance values. This indicates clearly that the instrument used had too wide a band width. Laboratories 6, 8, and 11 are low at one end of the wave band scale and high at the other. This would indicate improper wavelength adjustment, which can be due to either a faulty didymium filter or to improper adjustment of the instrument before use.

Examination of Figure 4 shows that the Beckman spectrophotometer gives higher values at the peak transmission and lower values at both the high and low wavelengths than does the Coleman Jr. This is primarily due to differences in band width, but stray light is responsible for differences at the extreme high and low wavelengths. The Beckman results peak at 502.5  $\mu$ , and the Coleman at 510  $\mu$ . Again this is attributable to band width. The results can be illustrated thus:

Coleman result at 510  $\mu$ . is essentially the average of Beckman readings at 510, 487.5, and 532.5  $\mu$ . or,

80.53	72.68 Calc.
66.50	72.64 Observed
71.00	0.04 Difference
3)218.03	
72.68	

likewise at 502.5  $\mu$ ., the average of 502.5, 480, and 525  $\mu$ ..

82.16	70.49 Calc.
57.80	70.77 Observed
71.50	0.28 Difference
3)211.46	
70.49	

The extent of the differences that can be expected between Coleman spectrophotometers is illustrated in

TABLE V  
NiSO<sub>4</sub> Solution Transmissions  
25 mm. "B" Cuvettes, no Added Acid, Water as Standard

Transmission	Instrument Number			
	A-1532	A-2084	A-1795	A-1693
400 $\mu$ .....	3.1	4.1	4.4	3.1
410 $\mu$ .....	2.8	4.0	4.3	2.9
420 $\mu$ .....	3.7	4.8	4.9	3.4
430 $\mu$ .....	4.8	7.0	6.9	4.9
440 $\mu$ .....	9.2	11.3	10.8	8.5
450 $\mu$ .....	16.7	17.1	17.4	14.6
460 $\mu$ .....	25.8	26.3	26.2	24.7
470 $\mu$ .....	37.8	37.7	37.6	36.0
480 $\mu$ .....	51.3	50.0	50.6	49.2
490 $\mu$ .....	63.0	60.7	62.3	60.9
500 $\mu$ .....	71.5	68.3	70.1	69.5
505 $\mu$ .....	73.3	70.0	72.0	72.4
510 $\mu$ .....	74.1	71.0	73.1	73.4
515 $\mu$ .....	73.2	70.5	72.9	73.4
520 $\mu$ .....	72.4	69.5	71.2	72.3
530 $\mu$ .....	67.8	65.4	66.4	67.8
540 $\mu$ .....	61.2	59.8	60.7	61.8
550 $\mu$ .....	55.1	52.9	54.6	55.4
560 $\mu$ .....	47.9	46.3	47.3	48.0
570 $\mu$ .....	40.2	38.4	39.9	40.3
580 $\mu$ .....	31.1	30.0	31.0	31.3
590 $\mu$ .....	22.5	22.3	23.0	22.7
600 $\mu$ .....	14.8	14.7	15.1	14.5
610 $\mu$ .....	9.2	9.4	9.5	9.0
620 $\mu$ .....	5.4	5.5	6.0	5.3
630 $\mu$ .....	3.3	3.5	4.0	3.2
640 $\mu$ .....	2.0	2.5	2.9	2.0
650 $\mu$ .....	1.5	1.9	2.4	1.5
660 $\mu$ .....	1.3	1.7	2.3	1.3
670 $\mu$ .....	1.3	1.6	2.3	1.4
680 $\mu$ .....	1.4	1.7	2.4	1.4
690 $\mu$ .....	1.5	2.0	2.3	1.5
700 $\mu$ .....	1.7	2.2	2.5	1.7

Table V, where a nickel sulfate solution is run by the four instruments, representing the extremes of manufacturing tolerances. It will be noted that machines A-2084 and A-1795, which have the most stray light, give the highest readings at low per cent transmission and that A-2084, which has the widest band width, shows the lowest transmission at the peak of the curve at 510  $\mu$ .

In Table VI are shown comparative data on nickel sulfate solution, using the four spectrophotometers with an additional comparison in which the instruments are activated on the one hand by a battery and on the other by a transformer. Very little can be

TABLE VI  
Coleman Transmission on Four Different Instruments  
Battery vs. Transformer  
25 mm. "B" Cuvettes, no Added Acid, Water as Standard

m $\mu$ .	Instru. A-1532	Instru. A-2084	Instru. A-1795	Instru. A-1693
	Bat. Trans.	Bat. Trans.	Bat. Trans.	Bat. Trans.
400.....	2.9 3.4	4.4 4.2	4.7 3.9	3.6 3.2
410.....	2.9 3.3	4.4 4.0	4.4 3.8	3.4 3.0
420.....	3.6 4.0	5.2 4.9	5.2 4.3	3.8 3.5
430.....	5.8 6.2	7.7 7.3	7.3 6.3	5.6 5.2
440.....	10.5 10.8	11.2 11.5	11.7 10.4	9.9 9.0
450.....	17.6 18.0	18.4 18.3	18.7 16.9	16.6 15.0
460.....	27.0 27.8	28.2 28.2	28.3 25.9	26.2 24.6
470.....	39.8 40.6	40.2 39.4	40.4 37.6	39.1 36.8
480.....	53.6 54.7	52.6 52.2	53.5 50.5	53.5 50.0
490.....	65.2 66.3	63.2 63.3	65.2 62.2	64.9 61.5
500.....	72.9 74.3	71.1 70.7	73.0 69.8	73.2 70.4
505.....	74.7 76.4	72.7 73.1	74.9 71.7	75.3 72.0
510.....	75.5 77.2	73.3 73.3	75.3 72.4	76.1 73.3
515.....	74.8 76.1	72.7 72.9	74.9 72.2	76.8 72.9
520.....	73.4 75.0	71.6 71.9	72.5 70.6	74.4 71.7
530.....	68.4 69.7	67.0 68.4	68.3 66.0	70.5 67.0
540.....	62.1 62.9	60.7 62.6	62.0 59.9	63.0 61.3
550.....	55.3 56.5	54.2 55.4	55.3 53.9	55.7 54.2
560.....	48.4 49.0	46.3 48.1	48.2 47.1	48.8 47.4
570.....	40.3 40.8	38.8 39.4	40.4 39.7	40.8 39.5
580.....	31.5 32.0	30.9 31.1	31.6 31.1	32.0 30.8
590.....	22.6 22.9	22.4 23.1	22.9 22.5	23.2 22.3
600.....	14.6 15.0	14.5 15.2	15.1 14.7	14.3 14.3
610.....	9.2 9.5	9.0 9.5	9.4 9.3	8.8 8.7
620.....	5.5 5.5	5.3 5.5	5.9 5.6	5.0 5.0
630.....	3.4 3.4	2.8 3.2	3.8 3.5	3.0 3.0
640.....	2.3 2.3	1.7 1.9	2.7 2.5	1.8 2.0
650.....	1.6 1.7	1.2 1.3	2.1 1.9	1.3 1.5
660.....	1.5 1.5	1.1 1.2	2.0 1.8	1.1 1.3
670.....	1.4 1.4	1.1 1.2	2.0 1.8	1.1 1.3
680.....	1.5 1.5	1.4 1.3	2.1 1.9	1.2 1.4
690.....	1.6 1.6	1.5 1.4	2.3 2.2	1.2 1.6
700.....	1.7 1.7	1.7 1.7	2.6 2.5	1.6 1.8

TABLE VII  
Daily Transmissions of NiSO<sub>4</sub> Solution  
(Using Storage Battery)

	New Soln. Made 9/16 pH 0.27			NiSO <sub>4</sub> +5 ml. HCl+H <sub>2</sub> O			Made 7/48 pH 1.02		
	NiSO <sub>4</sub> +5 ml. H <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O						NiSO <sub>4</sub> +5 ml. H <sub>2</sub> SO <sub>4</sub> +H <sub>2</sub> O		
	470	510	550	470	510	550	470	510	550
Sept. 16.....	40.5	75.7	55.4	40.7	76.7	56.5	40.3	76.2	55.7
				41.8	77.5	56.9	41.3	77.3	56.3
Sept. 17.....	41.0	75.4	56.0	42.1	77.7	56.9	41.6	77.2	56.1
	42.2	78.4	57.3	43.7	80.3	58.7	43.2	79.8	58.0
Sept. 20.....	39.2	74.4	55.4	39.7	75.8	56.5	39.4	75.4	55.8
	38.2	73.6	54.3	39.8	76.3	56.4	39.3	75.7	55.7
Sept. 21.....	39.0	74.2	55.2	39.9	76.0	56.5	39.5	75.4	55.9
	38.7	74.4	54.9	39.8	76.4	56.3	39.5	75.8	55.7
Sept. 22.....	39.0	74.6	55.0	40.2	76.4	56.4	39.7	75.8	55.7
	39.5	74.6	55.2	40.4	76.3	56.5	40.0	75.8	55.7
Sept. 23.....	39.4	74.8	55.1	40.3	76.4	56.3	39.8	75.8	55.6
	39.4	74.6	55.3	40.3	75.9	56.6	39.7	75.6	55.9
Sept. 24.....	38.8	74.8	55.5	39.7	76.2	56.6	39.2	75.6	55.8
	39.0	75.2	55.4	39.8	76.3	56.7	39.4	75.7	55.9
Sept. 27.....	39.3	75.6	55.4	40.0	76.7	56.4	39.5	76.1	55.7
	40.0	75.7	55.6	40.8	77.2	56.6	40.3	76.6	55.8
Sept. 28.....	39.8	76.1	56.1	40.8	77.3	57.2	40.3	76.8	56.4
	40.6	76.3	56.0	41.4	77.5	57.2	40.8	76.8	56.5
Sept. 29.....	40.1	76.2	55.8	40.8	77.4	57.0	40.3	76.9	56.3
	40.2	76.4	55.7	41.4	77.6	56.9	40.6	77.0	56.2
Sept. 30.....	40.2	76.0	56.3						
Average.....	39.7	75.4	55.6	40.7	76.9	56.8	40.2	76.4	56.0
Std. Deviation....	.562	1.05	.607	.984	.983	.526	.948	.996	.524

concluded from these data as to the relative merits of using a battery or a transformer.

In order to check the reproducibility of a single operator on a single instrument three nickel sulfate solutions were prepared, put into stoppered cuvettes, and measured morning and afternoon until 20 readings were taken.

These solutions were all acidified, two of them with sulfuric acid and one with HCl, to prevent any precipitation from occurring during the period of the observation. The measurements made are shown in

Table VII. It will be noted that the average results obtained are higher when HCl is used than when sulfuric acid is used and all the acidified samples give higher peak values than those obtained by the Committee where no acid at all was used. Standard deviations at 470, 510, and 550 m $\mu$ . vary from 0.5 to 1.05. This is about one-half of the deviation found between the various laboratories on both nickel sulfate and oil samples.

### Conclusions

The data completed on oils and on nickel sulfate solutions indicate that there is a standard deviation of up to 2% transmittance between measurements made by different laboratories on different instruments. This standard deviation is decreased by one-half when measurements are made by a single laboratory on a single instrument. The data indicate that nickel sulfate may be a satisfactory solution to use in standardizing the instruments in use in the various laboratories.

The results obtained on the 12 oils submitted for readings indicate that about the same degree of reliability is obtained spectrophotometrically as with the Lovibond system at low color levels. At high color levels the spectrophotometer shows considerably more reproducibility.

It is impossible to tell from the data obtained whether a single number system, such as a density measurement of 550 m $\mu$ ., or a color index value, consisting of some function of measurements at two or more wavelengths, would be the most suitable for general measurement.

PROCTER THOMSON, R. C. STILLMAN.

## Letter to the Editor

### On the Use of Sodium Carboxymethyl Cellulose as a Detergent, Especially as Combined with Fatty Acid Soap

DEAR SIR:

In the paper by Thomas H. Vaughn and Clifton E. Smith (Journal of A.O.C.S., Vol. 25, No. 2, Feb. 1948, p. 44) it is stated that, judging from published information, the applicability of sodium carboxymethylcellulose to the field of detergency appears relatively unknown in the U.S.A. Therefore it might be of interest to your readers to know something about the use of Na-C.M.C. in the Netherlands (Holland).

Owing to the scarcity and high prices of animal and vegetable oils and fats, the percentage composition of washing preparations and their allotment had been prescribed by the Government Office for Chemical Products (Rijksbureau voor Chemische Producten). Since May 1, 1948, the washing powder for laundries should contain: 12% of fatty acid (such as sodium soap), 1.25% of Na-C.M.C., and 40% of soda ash. Before this date the composition was: 21% of fatty acid (as sodium soap) and 35% of soda ash. In both cases the remainder (difference from 100%) is water.

The change in composition of the washing powder for laundries has been proposed by Mr. Smit, Direc-

tor of the Experimental Station for Laundering (Proefstation voor de Wasindustrie) at Delft. The proposal was based on the results of theoretical and experimental research, carried out at the Laboratory of the Experimental Station for Laundering.

In the Netherlands laundries most of the white work (cotton, linen, rayon) is washed together. This classification therefore includes sheets, pillow slips, body linen, towels, table cloths, tea-cloths, and rubbing cloths, etc.; but neither white shirts nor white coveralls are included in it.

Before the war it was regarded as normal if 1.5 lb. of soap (80% fatty acid) and either 2.4-3.6 lb. of soda ash or 1.6-2.4 lb. of metasilicate were used per 100 lb. of average soiled white work. Our research has shown (1) that it is possible to replace at least 0.75 lb. of the soap by 1.2 oz. of a good quality Na-C.M.C. (calculated as pure, dry substance). The results with three-fourths lb. of soap (80% fatty acid) plus 1.2 oz. of Na-C.M.C. are even better than with 1½ lb. of the same soap, the hardness of the water used varying from 0 to 120 p.p.m. (as CaCO<sub>3</sub>). Formerly a decrease in reflectivity for white light of 10% for originally clean test pieces, laundered 25 times together with this white work classification, was considered to be satisfactory. Nowadays, with only half the amount of fatty acid soap, which was used