TABLE VI

Properties of a Few Representative Dehydrated Castor Oils

	Ref. Index at 25°C.	Acid [1] Value	Acetyl Value	Viscosity (Gardner-Holdt)	Color [2] (Gardner)	Percent Diene Conjugation	Set-to-touch Time
Commercial (1)	1.4808	5.8	42.1	G+	6	26.8	2' 30"
Commercial (2)	1.4813	3.3	22.9	G	4	26.3	1' 45"
Commercial (3)	1.4809	4.1	25.3	G	5-6	27.0	1' 45"
Commercial (4)	1.4809	4.8	28.3	I	7-8	23.8	2' 5"
Continuous (1)	1.4812	8.6	32.2	E	7	31.5	1' 55"
Continuous (2)	1.4815	10.3	28.6	E	9	29.2	2' 15"

[1] The acid values of our dehydrated oils are high, possibly because of the poor vacuum employed.
[2] The Gardner color values must be taken with reservation as some of the oils could not be accurately matched with the standards.

acetyl value, and per cent conjugation on the drying time of the representative oils is given. It is evident from these results that there is little or no correlation between the various factors and drying time.

A comparison was made of the properties of two oils dehydrated continuously with several commercial dehydrated castor oils. The results are given in Table VI. In addition, 54-gallon Limed Rosin varnishes were prepared from these oils. In general, only slight differences were detected among the set-to-touch times, hot and cold water, and alkali resistance. However, the varnishes prepared, using the continuously dehydrated oils, produced significantly harder films.

Summary

A process for dehydrating castor oil continuously has been presented. The method consists essentially of exposing the oil in a thin film under the vacuum to temperatures between 310° and 350°C. for short periods of time in the presence of a dilute sulfuric acid catalyst. The relationship between various operational conditions and the physical constants of the oil produced has been determined. In addition, the oils were compared with several representative commercial oils.

REFERENCES

1. Block, H. S., U. S. Patent 2,380,720 (July 1945).
2. Colbeth, I. M., U. S. Patent 2,392,119 (Jan. 1946).
3. Fokin, S., J. Russ. Phys. Chem. Soc., *46*, 224, 1027 (1914); C. A. *8*, 2550 (1914); *9*, 1898 (1915).
4. Greaves, J. H., Oil Colour Trades J., *100*, 485 (1941).
5. Krafft, F., Ber., *21*, 2731 (1888).
6. Mikusch, J. D. von, Am. Paint J., *24*, 18, 20-21 (1940).
7. Ogg, C. L., Porter, W. L., and Willits, C. O., Ind. Eng. Chem., Anal. Ed., *17*, 394 (1945).
8. Rheineck, A. E., and Crecelius, S. B., U. S. Patent 2,415,969 (Feb. 1947).
9. Scheiber, J., Farbe u. Lack, *1929*, 153; Brit. Patent 306,452 (Feb. 1928); German Patent 513,540 (1930).
10. Ufer, H., German Patent 529,557 (1931); U. S. Patent 1,892,258 (Dec. 1932).
11. West, E. S., Hoagland, C. L., and Curtis, G. H., J. Biol. Chem., *104*, 627 (1934).

Report of the Color Committee

Spectrophotometric Color Grading

Review of Previous Work

DURING the past several years the situation with respect to obtaining Lovibond type color glasses has grown steadily worse. On December 12, 1947, A. J. Fawcett, in a letter to R. R. King, writes, "we are therefore advising our U.S.A. customers that we regret we must cancel all orders outstanding on our books for loose glasses." This final word puts it squarely up to the committee to eliminate once and for all the Lovibond system for measuring oil colors, especially where grading for trading purposes is involved. The Lovibond system has served a useful and needed purpose but, as tools, visual colorimeters using Lovibond color glasses are outmoded by the recent advances in scientific instruments. Past reports of the Color Committee have indicated that photoelectric colorimeters can be used successfully to grade oils and, where necessary, a translation to Lovibond red colors can be accomplished. There are certain drawbacks to any scientific instrument, and in the past cooperation of instrument makers with the Color Committee has left much to be desired. Hence no specific recommendation has been made by the Color Committee since it has felt that no well standardized filter-photocell instrument was available on the market.

During the past year or two there has been a decided tendency toward the use of a spectrophotometer for measuring oil colors. This is because the spectrophotometer produces fundamental data amenable to all sorts of color analyses. The development of simple, photoelectric instruments, which are easy to manipulate as well as inexpensive, has also been a decided factor in extending the use of spectrophotometers in color measurements. It is the purpose of this report to present some of the data relative to oil colors which has been obtained by using the Coleman Model 6A spectrophotometer and to suggest a method whereby spectrophotometric data may be used to replace all measurements now made using the Lovibond system. It is hoped that additional cooperative work will lead to a finished method that will be adopted by the Uniform Methods Committee of the Society.

Work Done

A recent model Coleman spectrophotometer, 6A Junior, was obtained from Coleman Instruments inc. Mr. Coleman points out that he is desirous of cooperating in every way with the committee in the design of the instrument, furnishing any number of instruments for committee use, and standardizing the instruments to committee specifications when and if such a time should come. This is an important point and well worth consideration in investigating any new instrument for use in widely different laboratories. Two companies, Swift and Company and Archer-Daniels-Midland, have had considerable experience with the Coleman spectrophotometer and have found the instruments quite satisfactory from an operation standpoint. These instruments are simply

TABLE I

Lab. and Wave Length	Sample No. and Transmissions								
	Oil Samples								
	1	2	3	4	5	6	7	8	9
P & G 400 mμ	14.5	19.6	7.8	3.2	3.2	37.3	16.0	4.3	16.4
B-A 400 mμ	14.4	20.0	8.2	3.2	3.1	36.1	16.1	4.8	16.0
Swift 400 mμ	18.8	24.0	12.0	5.0	4.8	39.5	21.4	6.8	17.0
Swift 400 mμ	17.5	22.8	10.5	4.5	4.5	38.6	19.7	6.0	18.8
P & G 540 mμ	90.5	91.0	90.8	48.6	46.8	94.5	92.5	73.8	84.3
B-A 540 mμ	91.8	92.2	92.1	48.0	44.8	95.2	93.1	73.3	84.3
Swift 540 mμ	91.2	91.0	92.0	52.3	51.3	94.5	93.2	73.8	83.5
Swift 540 mμ	92.0	92.2	92.9	52.0	49.8	95.0	93.8	75.8	85.0
P & G 670 mμ	98.0	95.2	97.6	59.8	58.7	93.0	96.5	90.1	82.2
B-A 670 mμ	99.0	96.8	98.1	60.5	58.0	94.0	97.2	91.1	82.2
Swift 670 mμ	99.3	98.3	100.0	62.5	62.8	97.2	100.0	92.8	85.2
Swift 670 mμ	99.0	98.0	99.5	65.0	62.8	96.0	99.2	94.0	86.5

19-mm. cuvettes, distilled water 100% transmission.

constructed, easy to manipulate and read, and extremely rugged. The instrument operates from line current or batteries, has a 35-mμ band width, and reads either transmission or optical density.

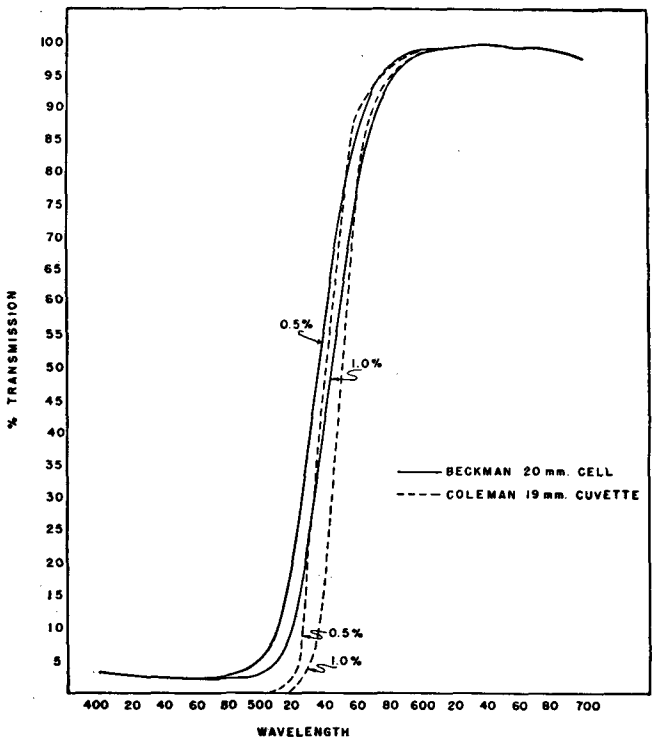
V. C. Mehlenbacher submitted nine oil samples to the Barrow-Agee Laboratories and to Procter and Gamble for comparative results, using the Coleman instrument. Results obtained are shown in Table I.

Mehlenbacher states that the difference in readings between his laboratory and Barrow-Agee and Procter and Gamble laboratories is apparently due to stray light and that his instruments are being returned to the factory to be overhauled and corrected. There apparently is no reason why any number of instruments cannot be made to read alike if the design is the same. Stray light probably cannot be eliminated entirely but can be reduced to and held at a minimum value for all machines.

A 1.0% or 0.5% $K_2Cr_2O_7$ solution in water would seem to be extremely useful in determining the amount of stray light in any and all instruments, perhaps also for other standardization purposes.

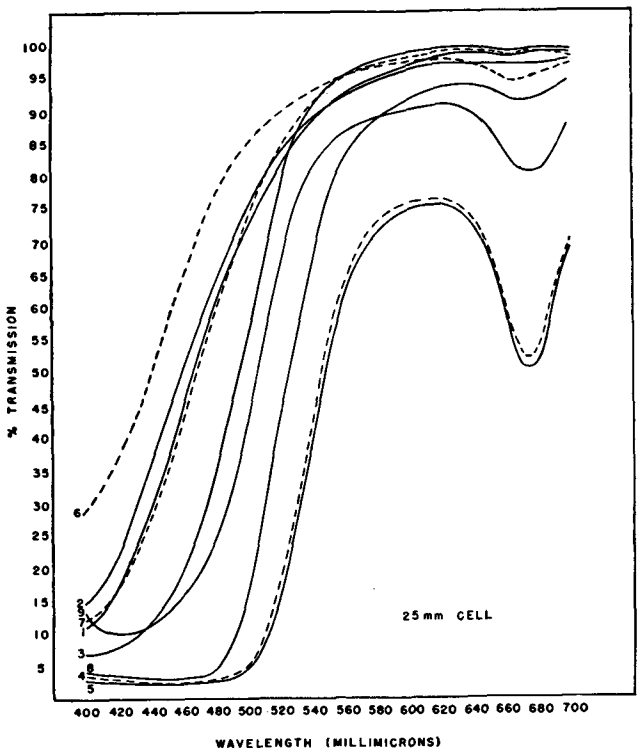
CURVE 1.

0.5% & 1.0% DICHROMATE SOLUTIONS



CURVE 2.

SWIFT OIL TRANSMISSIONS



Curve 1 shows the transmission of 1.0% and 0.5% $K_2Cr_2O_7$ solutions as determined in 19-mm. cuvettes in the Coleman instrument and 20-mm. square cells in the Beckman spectrophotometer. It seems logical to assume from a study of these curves that the Coleman instrument has about 2.5% of stray light since the curves level off at the 2.5% transmission level. Readings taken with a 25-mm. cuvette show only about 1.0% stray light using a 1.0% $K_2Cr_2O_7$ solution. This may well indicate that in so far as possible the use of very small cells should be avoided.

Nine oils prepared by G. W. Agee were read by the Barrow-Agee Laboratory and the Procter and Gamble Laboratory. The data are shown in Table II.

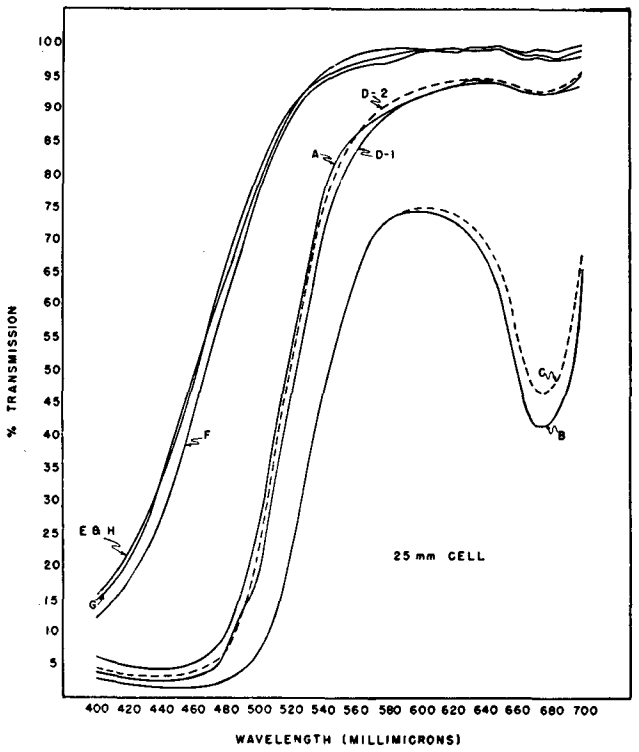
The transmissions on the Swift and Agee oils shown in Tables I and II were determined, using 19-mm. cuvettes. These same oils were examined, using a 25-mm. cuvette which is the largest cuvette which can be used in the Coleman instrument. The transmission curves are shown in Curves 2 and 3.

The 18 Swift and Barrow-Agee oils were arranged in order by eye and a number assigned to each oil.

From the transmission curves a weighted transmission $T^1 = \frac{0.3\,(T500) + 1.0\,(T550) + 0.3\,(T620)}{1.6}$ was determined for each oil and from this weighed T^1 a corresponding weighed color density D^1. This particular weighting was used because, at the 500-mμ. and 620-mμ. wave lengths, the effect on the eye is about 0.3 as much as at 550 mμ. Table III shows the values for each of the oils as well as the ordered arrangement under each of the categories listed.

CURVE 3.

BARROW-AGEE OIL TRANSMISSION



Spearman-Brown rank order correlations have been calculated between eye orders and the other orders except T^1 using the formula $r = 1 - \frac{6\Sigma d^2}{N(N^2-1)}$. The values calculated are:

$r = 0.95$ between eye and Lovibond red order

$r = 0.93$ between eye and color density at 550 mμ.

$r = 0.95$ between eye and D^1

These values of r are all high. The differences are insignificant since the actual real value cannot be determined on such a small number of samples. The only inference that can be drawn is that it makes but little difference which system is used if the eye is used as the final criterion.

The color of a large number of samples of oil has been read by the Lovibond system with the Coleman spectrophotometer at 550 mμ. in a 25-mm. cuvette, using carbon tetrachloride as a standard. Part of the readings made are tabulated in Table 4. The data are plotted in Curves 4 and 5. These data indicate quite clearly that Lovibond red colors may be easily estimated from color density values at 550 mμ., except in the case of green oils where low Lovibond values are obtained. It also appears to be immaterial whether straight oil or a carbon tetrachloride dilution of the oil is used.

The effect of temperature and comparison liquid was studied briefly. In Curve 6 is shown the relative transmission curves obtained, using carbon tetrachloride and tetrachlorethane as standards. Values are shown for the oil at 25°C., 50°C., and 100°C. It seems likely that the temperature of the fat is relatively unimportant and that only slightly different readings are obtained against carbon tetrachloride and tetrachlorethane. Since carbon tetrachloride is much easier to obtain and holds its color much better, it is suggested as the preferable standardizing liquid. The refractive index of lard, tallow, soybean, and cottonseed oils is 1.46 to 1.47. Coconut oil and palm kernel oil may run as low as 1.44. Carbon tetrachloride has a refractive index of 1.463.

Curve 7 represents a dark tallow sample diluted with a light fatty acid and with carbon tetrachloride. This confirms results in Curves 4 and 5, in which diluted samples were found to fall on the same curve as undiluted samples. The effect of diluting fat samples with CCl_4 is shown also in Curve 8. Here we see that practically a straight line is obtained when a sample of tallow or cottonseed oil is diluted with CCl_4 and the per cent fat is plotted against the density at 550 mμ.

One of the chief difficulties encountered in the use of the Lovibond system is in reading the color of dark oils where a 5¼-inch column becomes too dark to match. The color is not proportional to the length of column measured as is shown in Curve 9. Nor is the Lovibond red color proportional to the dilution as is shown in Curve 10.

Conclusions

Data have been presented showing that:

1. The Lovibond color system is in many respects obsolete and must be replaced.
2. The spectrophotometer can be used easily to read

TABLE II

Mark	Material	Lovibond Color	Millimicrons					
			400		540		670	
			BA	P&G	BA	P&G	BA	P&G
A	Refined Cottonseed Oil	35 Y - 5.7 R	10.0	9.6	81.0	80.2	95.0	94.4
B	Refined Cottonseed Oil	35 Y - 8.3 R	3.5	2.9	52.0	53.5	55.5	52.3
C	Refined Cottonseed Oil	35 Y - 8.2 R	3.5	3.1	52.5	54.5	60.0	56.8
D-1	Cottonseed Oil (Refined Regular Meth.)	35 Y - 7.5 R	5.5	4.8	74.5	76.0	95.0	95.3
D-2	Cottonseed Oil (Refined Expeller Meth.)	35 Y - 6.4 R	6.5	6.3	77.5	79.2	95.5	95.4
E	Refined, Bleached Soybean Oil	15 Y - 1.5 R	21.0	22.4	96.0	95.3	99.5	99.1
F	Refined, Bleached Soybean Oil	19 Y - 1.9 R	16.5	17.6	95.0	94.6	99.0	99.0
G	Refined, Bleached Soybean Oil	17 Y - 1.7 R	20.0	22.3	95.5	95.5	99.0	98.8
H	Refined, Bleached Soybean Oil	15 Y - 1.5 R	21.0	23.0	96.0	95.6	99.0	99.0

Readings made on a Coleman Model 6-A Junior Spectrophotometer, using the 19 x 105-mm. cuvettes. Instrument set on 100% transmission with a cuvette containing distilled water.

TABLE III

Composite Data on Swift and Barrow-Agee Oils

Oil	Color	Lovibond Red	Den. at 550 mμ.	T^1	D^1	Eye Grading	Order				
							Lov.R	Den.550	T^1	D^1	Eye
Swift											
1	Normal	3.7/35	.0434	88.3	.0539	8	10	9	8	8	8
2	Normal	3.1/30	.0429	88.8	.0516	3	6	8	7	7	3
3	Normal	3.5/35	.0306	87.0	.0605	9	8.5	6	9	9	9
4	Green	11.5/70	.2717	48.4	.3152	17	17	17	17	17	17
5	Green	12.8/70	.2907	46.9	.3288	18	18	18	18	18	18
6	Normal	1.6/16	.0260	92.0	.0362	1	3	5	5	5	1
7	Normal	3.3/30	.0315	90.3	.0442	7	7	7	6	6	7
8	Normal	9.1/70	.1124	68.3	.1656	14	16	14	14	14	14
9	Green	3.5/30	.0742	77.6	.1103	10	8.5	10	10	10	10
B-Agee											
A	Normal	5.7/35	.0786	74.5	.1279	11	11	11	11	11	11
B	Green	8.3/35	.2480	50.0	.3010	15	15	15	16	16	15
C	Green	8.2/35	.2482	50.5	.2967	16	14	16	15	15	16
D-1	Normal	7.5/35	.1051	69.4	.1587	13	13	13	13	13	13
D-2	Normal	6.4/35	.0888	72.6	.1391	12	12	12	12	12	12
E	Normal	1.5/15	.0164	93.6	.0287	4	1.5	1	1	1	4
F	Normal	1.9/19	.0181	92.7	.0329	6	5	3	4	4	6
G	Normal	1.7/17	.0177	93.2	.0306	2	4	2	2	2	2
H	Normal	1.5/15	.0185	93.1	.0310	5	1.5	4	3	3	5

the color of oils and can be expected to give reproducible results between laboratories.

3. Single color density readings at 550 mμ., using a 25-mm. cuvette and carbon tetrachloride as a comparison medium, are a better measure of color than are Lovibond red values. Density values may be translated into Lovibond red values by means of a curve.

4. A straight line color system will result by using 550-mμ. color densities and diluting dark colors to enable measuring.

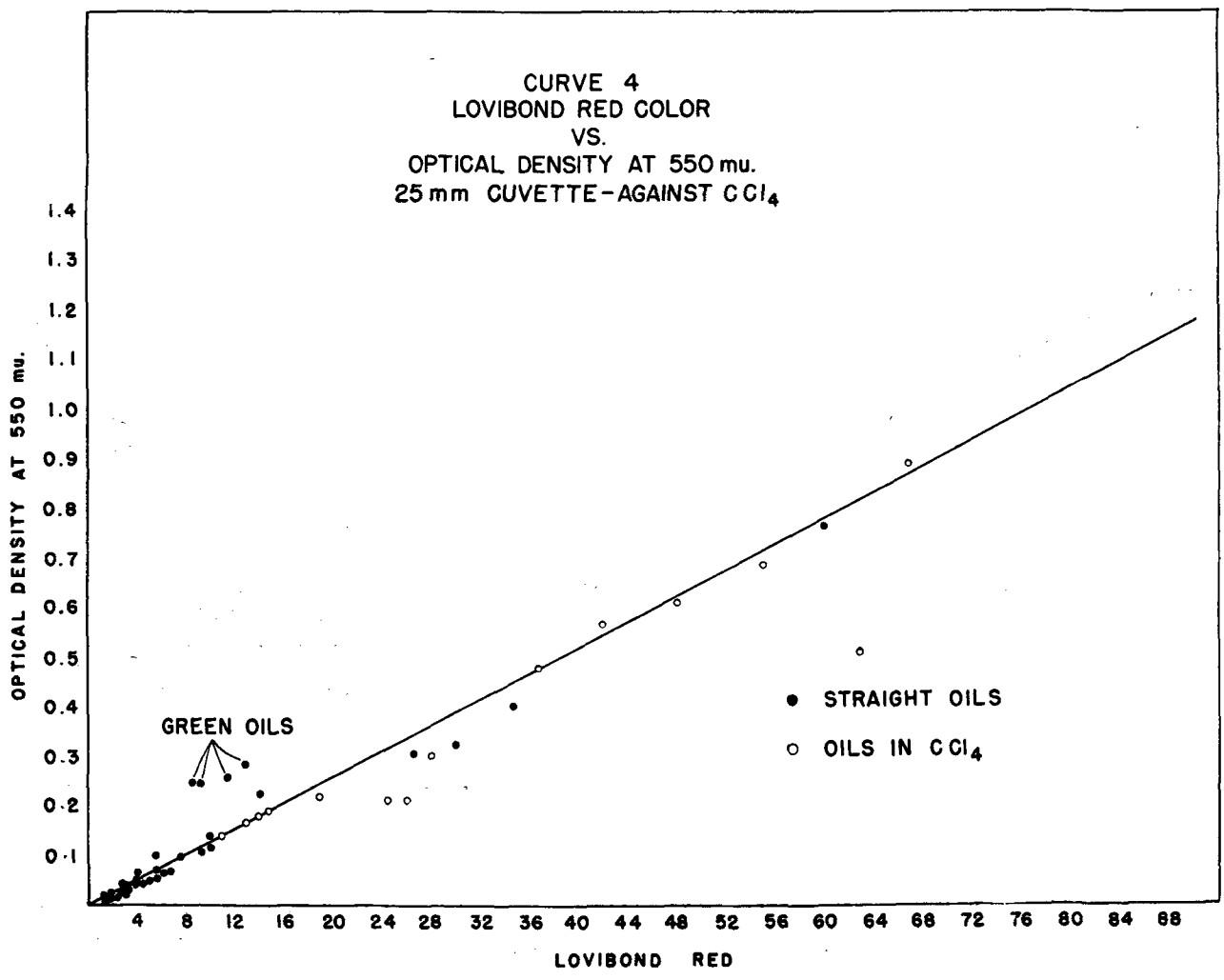
Method

The method, as used in this work, follows. It should be clearly understood that this method is a preliminary one, bears no A.O.C.S. approval, and may be changed in accordance with future committee findings.

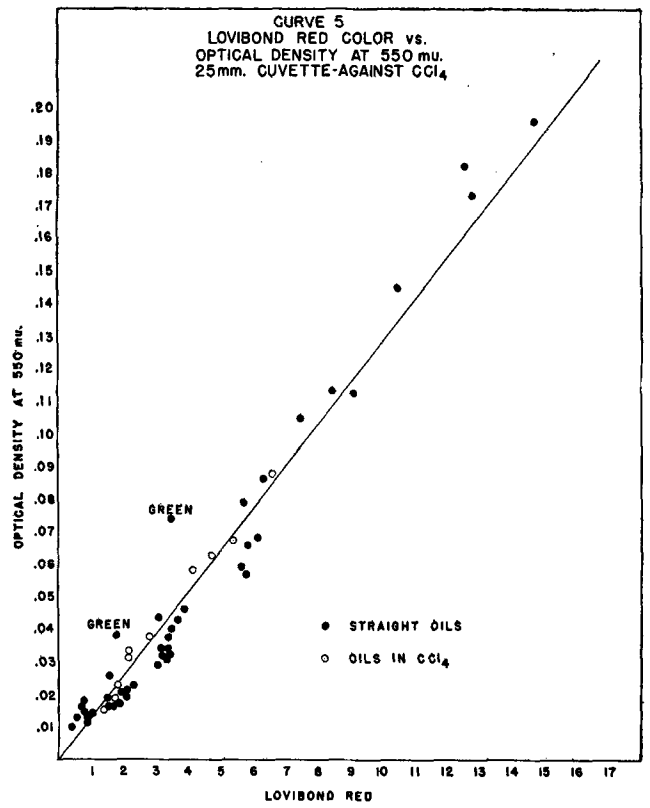
A. APPARATUS

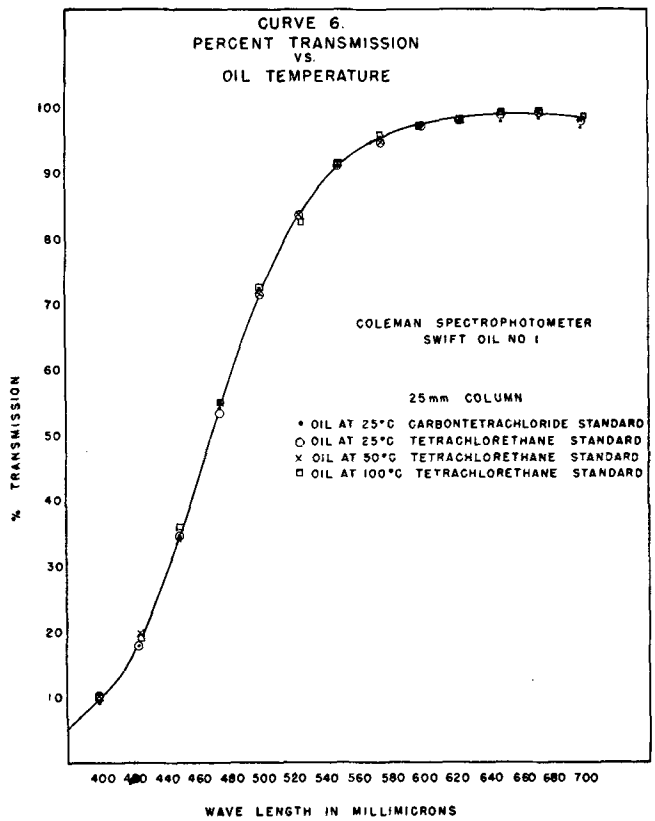
1. Spectrophotometer

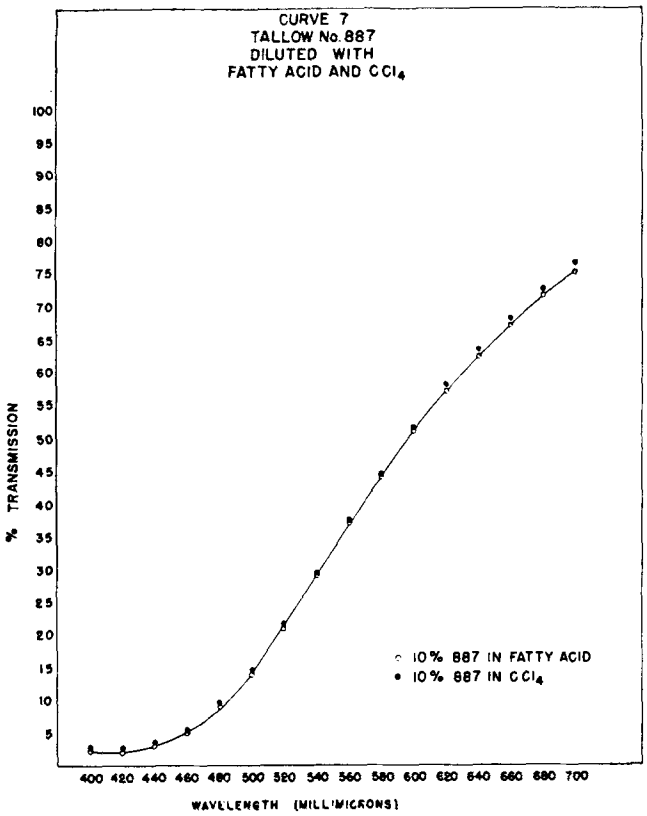
a. Coleman Model 6A Junior, or any other spectrophotometer with a 35-mμ. band spread.

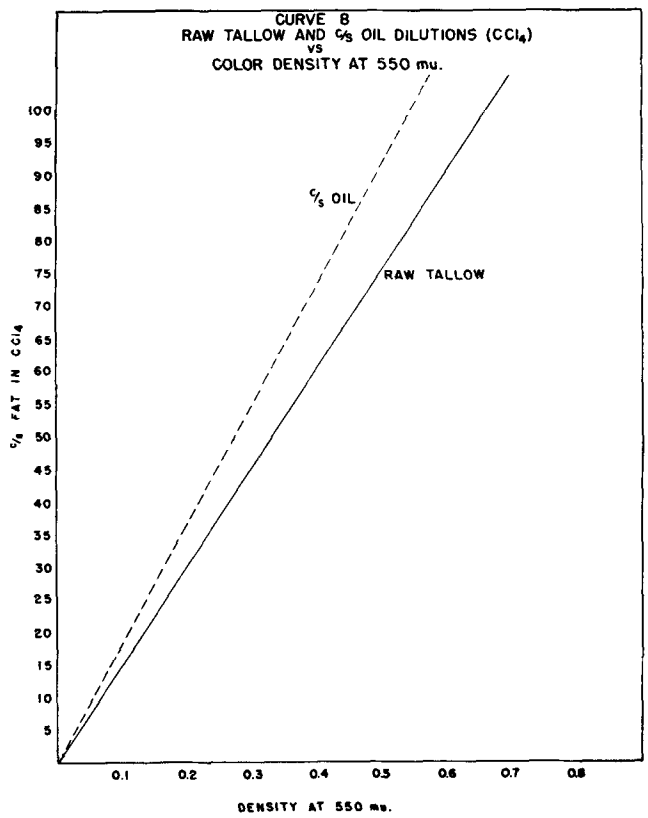


2. Matched glass cells or cuvettes, 21.3 ± 0.1 mm. inside diameter. The cells or cuvettes should be kept clean and free from scratches.
3. Standardizing filters.
4. Filter paper, fine porosity, such as E & D No. 192, Whatman No. 12, Reeve-Angel No. 870, or S & S No. 596.









B. REAGENTS

1. C. P. carbon tetrachloride. If not water white, it should be redistilled.

C. PROCEDURE

1. The sample must be absolutely clear. If not, filter through a specified paper at a temperature of at least 10°C. above the melting point of the fat. The sample

TABLE IV

Lovibond Red and Densities at 550 mμ.
(25-mm. Cuvette—Against CCl_4)

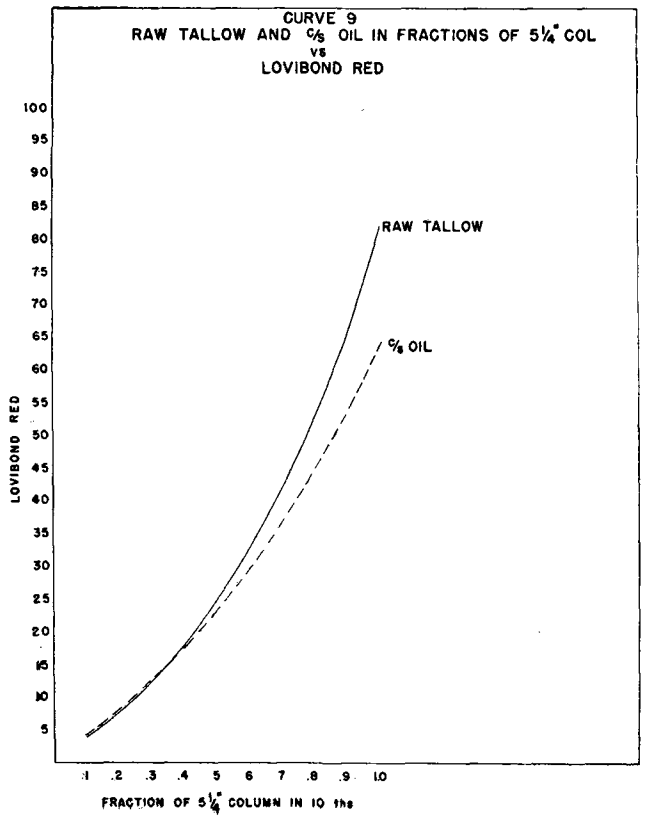
Fat	Lov. Red	Den. 550 mμ	Fat	Lov. Red	Den. 550 mμ.	Fat	Lov. Red	Den. 550 mμ.
Swift No. 1	3.7	.0434	Ref. & Bl. Veg. Oils	2.0	.0200	Refined Veg. Oils	3.0	.033
Swift No. 2	3.1	.0429	Ref. & Bl. Veg. Oils	3.1	.0292	Refined Veg. Oils	12.6	.183
Swift No. 3	3.5	.0306	Ref. & Bl. Veg. Oils	1.8	.0186	Refined Veg. Oils	5.3	.0680
Swift No. 4*	11.5	.2717	Ref. & Bl. Veg. Oils	3.4	.0338	Refined Veg. Oils	4.4	.0706
Swift No. 5*	12.8	.2907	Ref. & Bl. Veg. Oils	3.4	.0315	Refined Veg. Oils	4.9	.0605
Swift No. 6	1.6	.0260	Ref. & Bl. Veg. Oils	2.2	.0209	10% Tallow in CCl_4	30.2	.33
Swift No. 7	3.3	.0315	Ref. & Bl. Veg. Oils	3.9	.0458	10% Tallow in CCl_4	14.3	.23
Swift No. 8	9.1	.1124	Ref. & Bl. Veg. Oils	3.3	.0338	10% Tallow in CCl_4	9.9	.15
Swift No. 9*	3.5	.0742	Ref. & Bl. Veg. Oils	2.1	.0186	10% Tallow in CCl_4	5.8	.106
B-Agee A	5.7	.0786	Ref. & Bl. Veg. Oils	2.1	.0200	10% Tallow in CCl_4	3.9	.076
B-Agee B*	8.3	.2480	Ref. & Bl. Veg. Oils	2.1	.0200	RB Oil—Crude Mixes	28.0	.308
B-Agee C*	8.2	.2482	Ref. & Bl. Veg. Oils	3.4	.0381	RB Oil—Crude Mixes	24.4	.264
B-Agee D-1	7.5	.1051	Ref. & Bl. Veg. Oils	3.5	.0396	RB Oil—Crude Mixes	18.7	.230
B-Agee D-2	6.4	.0888	Ref. & Bl. Veg. Oils	0.9	.0129	RB Oil—Crude Mixes	14.8	.197
B-Agee E	1.5	.0164	Ref. & Bl. Veg. Oils	8.5	.1135	RB Oil—Crude Mixes	12.8	.174
B-Agee F	1.9	.0181	Ref. & Bl. Veg. Oils	5.8	.058	RB Oil—Crude Mixes	10.5	.143
B-Agee G	1.7	.0177	Ref. & Bl. Veg. Oils	6.2	.068	10% Crude Oil in CCl_4	1.4	.0159
B-Agee H	1.5	.0185	Ref. & Bl. Veg. Oils	5.9	.067	10% Crude Oil in CCl_4	1.8	.0191
Ref. & Bl. Veg. Oils	0.7	.015	Ref. & Bl. Veg. Oils	1.7	.038	10% Crude Oil in CCl_4	1.9	.0223
Ref. & Bl. Veg. Oils	0.8	.010	Ref. & Bl. Veg. Oils	5.7	.059	10% Crude Oil in CCl_4	2.2	.0315
Ref. & Bl. Veg. Oils	0.7	.016	Ref. & Bl. Veg. Oils	2.1	.0223	10% Crude Oil in CCl_4	2.2	.0334
Ref. & Bl. Veg. Oils	0.9	.012	Ref. & Bl. Veg. Oils	4.2	.0530	10% Crude Oil in CCl_4	2.9	.0376
Ref. & Bl. Veg. Oils	0.8	.013	Ref. & Bl. Veg. Oils	4.4	.0570	10% Crude Oil in CCl_4	3.7	.0482
Ref. & Bl. Veg. Oils	0.4	.010	Ref. & Bl. Veg. Oils	3.4	.0338	10% Crude Oil in CCl_4	4.2	.0575
Ref. & Bl. Veg. Oils	0.6	.013	Ref. & Bl. Veg. Oils	4.3	.0482	10% Crude Oil in CCl_4	4.8	.0615
Ref. & Bl. Veg. Oils	0.7	.018	Ref. & Bl. Veg. Oils	4.1	.0400	10% Crude Oil in CCl_4	5.5	.0685
Ref. & Bl. Veg. Oils	0.6	.013	Ref. & Bl. Veg. Oils	3.5	.0338	10% Crude Oil in CCl_4	6.7	.0888

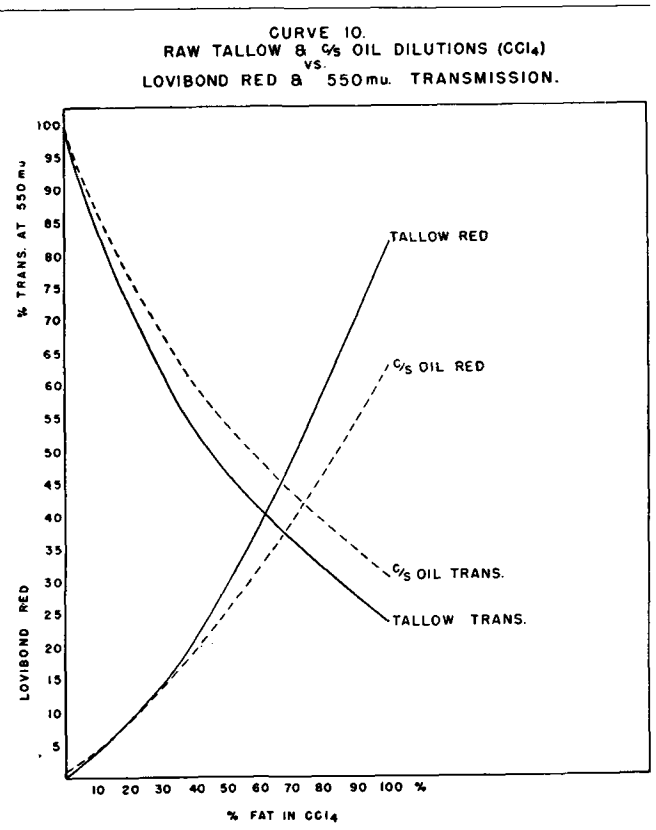
* Designates green oils.

should not be held melted longer than necessary since darkening may occur.

2. Adjust the spectrophotometer to read the zero and 100% transmission points correctly and read the calibrating filters. Adjust the instrument to give the correct readings, following manufacturer's instructions.
3. Set the wave length scale to 550 mμ.
4. Recheck the zero reading of the instrument and set the 100% transmission point exactly with a tube filled with CCl_4 in the instrument.
5. Fill a sample tube with the sample, using a sufficient amount to insure a full column of oil in the light beam.
6. Place the filled tube in the instrument and read the optical density to the nearest 0.001 from the scale.
7. If the reading is above 0.700, dilute 10 ml. of the sample to 100 ml. with CCl_4, mix thoroughly, filter if necessary, and reread. Multiply the reading obtained by 10.
8. If the diluted sample still has a reading above 0.700, dilute 10 ml. of the sample-CCl_4 mixture to 100 ml. with more CCl_4. Mix thoroughly, and reread. Multiply the reading obtained by 100.
9. Approximate Lovibond red values may be obtained by use of the equation:

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





NOTE: The 25-mm. and 19-mm. cuvettes used in this work had internal diameters of 21.3 mm. and 16.1 mm., respectively.

G. W. AGEE, *chairman.*