Reid, W. D., Swift & Co., Chicago.
Richert, Dr. T. G., Albert H. Bruecke, New York City.
Richie, H. B., Swift & Co., Chicago.
Roberts, P. B., Hild Floor Machine Co., Chicago.
Rooney, F. M., Precision Scientific Co., Chicago.
Roschen H. L., Swift & Co., Chicago.
Rupp, Virgil R., Kingan & Co., Indianapolis, Ind.
Ruston, N. A., Emery Industries, Inc.

Sandtner, J. S., Swift & Co., Chicago.
Sandy, D. D., Wadhams Oil Co., East Chicago, Ind.
Schaar, A. E., Schaar & Co., Chicago.
Schille, J. L., Best Foods, Inc., Chicago.
Schroder, Arthur, Pure Oil Co., Evanston, Ill.
Schuette, H. A., University of Wisconsin, Madison, Wis.
Sharples, W. P., Sharples Specialty Co., Philadelphia, Pa.
Sheely, M. L., Armour Soap Works, Chicago.
Shipner, J. R., Cudahy Packing Co., South Omaha, Nebr.
Sipple, H. L., American Can Co., Maywood, Ill.
Shortal, C. F., Schutte & Koerting Co., Chicago.
Sieck, Herbert, Sieck & Drucker, Inc., Chicago.
Siegel, E. A., Lever Bros. Co., Hammond, Ind.
Skarda, W. C., Lever Bros. Co., Hammond, Ind.
Sorensen, S. O., Archer-Daniels-Midland Co., Chicago.
Spannuth, H. T., Wilson & Co., Chicago.
Spielman, L. A., Durkee Famous Foods, Chicago.
Stanger, O. C., Miner Laboratories, Chicago.
Starkie, Frank L., Thomas E. O'Neill Co., Chicago.
Stauffer, Chas. E., R. R. Street & Co., Chicago.
Steineker, C. M., Durkee Famous Foods, Louisville, Ky.
Stern, Paul L., Clinton Company, Clinton, Iowa.
Stingley, D. V., Armour & Co., Chicago.
Stockmann, G. J., Wurster & Sanger, Inc., Chicago.
Stucker, Jos. B., Pure Oil Co., Chicago.
Sutker, L. L., Wilson & Co., Chicago.

Taylor, W. L., Archer-Daniels-Midland Co., Chicago.
Tefft, H. D., Institute of American Meat Packers, Chicago.
Thornton, M. H., Purdue University, West LaFayette, Ind.
Todd, Van Winkle, Hanson Van Winkle Mining Co., Matawan, N. J.
Tolman, L. M., Wilson & Co., Chicago, Ill.
Trainor, Geo. W., Darling & Co., Chicago.
Trusler, R. B., The Davies-Young Soap Co., Dayton, Ohio.

Vahlteich, H. W., The Best Foods, Inc., New York City.
Van Zile, B. S., Colgate-Palmolive-Peet Co., Jersey City, N. J.
Vibrans, F. C., Institute of American Meat Packers, Chicago.
Voorhees, Vanderveer, Standard Oil Co., Chicago.

Wannamaker, T. R., Southern Cotton Oil Co., Chicago.
Wilcox, H. C., Swift & Co., Chicago.
Wilkins, Chas. E., Best Foods, Inc., Chicago.
Wrench, Jos., Industrial Chemical Sales Division, New York City.
Wood, Arthur H., Corn Products Refg. Co., Argo, Ill.
Wright, R. E., Lever Bros., Hammond, Ind.
Wurster, O. H. Wurster & Sanger, Inc., Chicago.

Young, L. E., L. E. Young Co.

Zebbs, Francis, Armour & Co., Chicago.
Zeigler, C. C. Swift & Co., Chicago.

NOTE ON THE SPECTROPHOTOMETRIC GRADING OF VEGETABLE OILS ON THE N" LOVIBOND SCALE*

By KASSON S. GIBSON**

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CONTENTS

ABSTRACT

On the basis of data published by McNicholas, it is shown that there is no significant correlation between the lightness or darkness of an oil and the Lovibond grade assigned to the oil by the practical color grader. The Lovibond color grade of a vegetable oil may therefore be computed from its spectral transmittance by colorimetric methods without taking into account the luminous transmittance of the oil. This method of grading might serve to settle disputes among the oil chemists as to the correct Lovibond grade of an oil.

I. INTRODUCTION

In 1935 McNicholas published a paper,[1] giving the spectral transmittances of 125 vegetable oils, 111 of which were from the cotton seed, together with the spectral transmittances of the various Lovibond glass combinations used in the commercial color grading of such oils, and illustrating the colorimetric values assigned to both the oils and the glasses on the basis of the O.S.A. observer and co-ordinate system.[2] He furthermore showed that some oils are much lighter, and some much darker, than Lovibond glass combinations of the same chromaticity, and that even if of the same lightness, or even if photometric means be employed to eliminate the brightness difference between the oil and the glasses in the colorimeter, there still remains in most cases a distinct chromaticity difference which no adjustment of Lovibond red will eliminate.

However, by graphical methods, based on work by Judd,[3] McNicholas was able to determine the Lovibond red numeral which in combination with the 35-yellow would give the closest chromaticity match for any given oil. He was thereupon enabled to compare the Lovibond grades of the oils thus determined from spectrophotometric data with the respective grades previously assigned to the oils by the donors according to the usual methods.

This paper by McNicholas is without question of fundamental importance in any future study of colorimetric methods of oil grading. Furthermore, the graphical method of deriving the Lovibond grade of an oil from spectrophotometric data may prove acceptable for use by a standardizing laboratory such as the National Bureau of Standards, in those cases where there is dispute among the chemists as to the Lovibond grade of an oil.

The question of the bureau's thus computing the N" grade of an oil from its measured spectral transmittance, and in this way serving as arbiter if this were desired by the oil chemists, was raised by Mr. L. M. Gill, Chairman of the A.O.C.S.

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color glass development committee, of which the author is a member. The answer depends on the satisfactory solution of certain other problems connected therewith. The present paper is an attempt to solve one of these problems on the basis of some of the data obtained by McNicholas.

II. COLOR GRADING OF VEGETABLE OILS ON THE N″ SCALE

The universal practice among American oil chemists is to grade the color of a 5¼ inch thickness of oil in terms of Lovibond red and yellow glasses.[4] In the grading of cottonseed oils the combination mostly used is 35-yellow and variable red. Unfortunately, as illustrated in previous bureau publications,[5] the consistency of the numerals on the red glasses was not satisfactory to the oil chemists and they requested the bureau to undertake the re-calibration of such glasses. This was accordingly done, the bureau first establishing by measurements on its own set of glasses a consistent additive scale known as the Priest-Gibson or N″ scale[6] and then regrading submitted glasses on this scale by direct comparison with its own standardized glasses. Whenever reference is made in this paper to the N″ scale, it should be remembered that this is a scale of Lovibond red glasses in combination with 35-yellow, the N″ numerals being those assigned the red glasses on this adjusted bureau scale. The original Lovibond numerals, engraved on the red glasses by the makers, are referred to as the N numerals.

In the development and establishment of the N″ scale at the bureau, the values of luminous transmission, which determine the lightness of the glass or combination of glasses, were disregarded, because assurance was given that the color-grade of an oil was determined on the basis only of its redness or greenness—that is, on the amount of Lovibond red, with 35-yellow, necessary to match the oil—and not on the basis of its lightness or darkness. A light and dark oil of the same redness would on this basis be given the same Lovibond grade.

If, in case of dispute among themselves, the oil chemists are satisfied to accept results on the basis of the graphical method used by McNicholas, designated hereinafter as the spectrophotometric method, in which the colorimetric results are derived by spectrophotometric measurements followed by colorimetric computations and in which the lightness or darkness of the oil is not taken into account, the method may be said to be already available. When, however, the question was raised by Mr. Gill, it was felt that if possible some test should be made to see whether or not the values of N″ derived by the spectrophotometric method should be weighted by some factor which would take into account the luminous transmittance of the oils. The test described in the following section was accordingly made.

III. EFFECT OF LIGHTNESS OF AN OIL ON ITS COLOR GRADE

To assist in a better understanding of the present results, two of the illustrations from McNicholas's paper are reproduced here, with slight additions. Fig. 1 is a reproduction of the upper part of Fig. 8 of that paper, the continuous line being extrapolated to N″ = 26.0. In this figure T_s is the sunlight transmittance of 5¼ inches of the oil, 0.892 T_s is the sunlight transmission of a 5¼ inch cell filled with the oil, and $-\log_{10} 0.892\ T_s$ expresses the transmission values on a scale such that equal vertical distances on any part of the scale are approximately proportional to equally discriminable differences when the oils are viewed in a colorimeter. The small solid circles and continuous line (dashed from 21.0 to 26.0) represent the sunlight transmissions of combinations of Lovibond glasses as noted. The continuous line, plotted through the points for three glasses (one 35-yellow with either two red glasses or one red and one clear glass) probably best represents the average lightness of the Lovibond glass combinations with which the oils are compared. Oils represented by points above this curve are lighter in color than the glasses, those below this curve are darker. The values of N″ for the oils plotted in this figure are as given in column 8 of Table 1 of the paper by McNicholas.

Figure 2 is a reproduction of Fig. 9 of this previous paper, the dashed line being added for the present publication. In this figure the values of N obtained by the donors are plotted against the values of N″ obtained by McNicholas by the spectrophotometric method. The dashed line is an attempt to make the comparison slightly more exact. Since the donors used un-

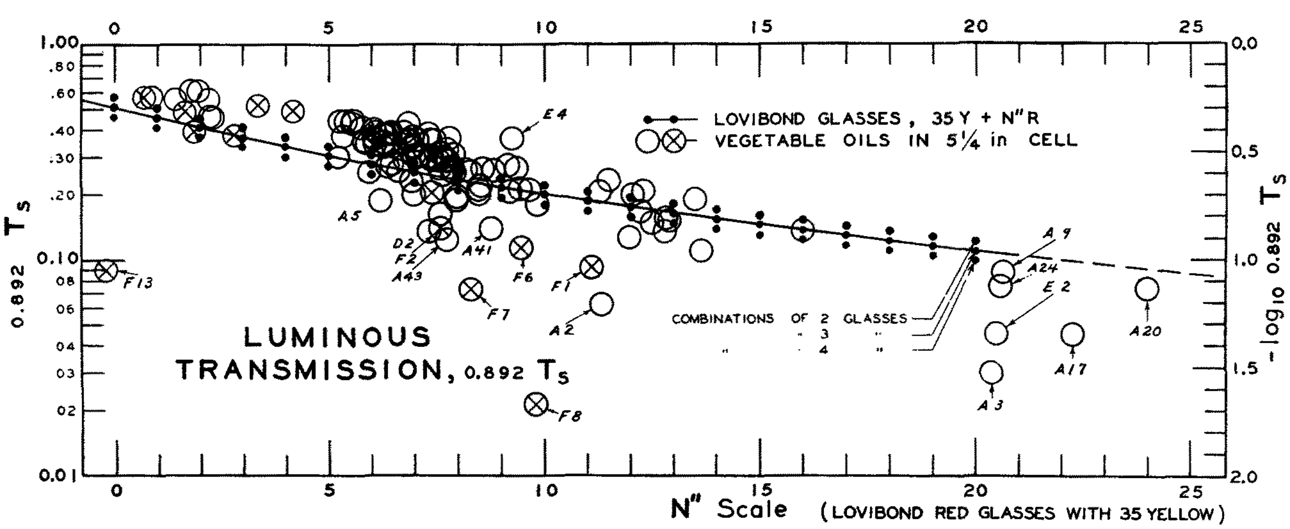

Fig. 1—This figure is the same as Fig. 8 (top) of the paper by McNicholas (Oil and Soap, 12, 167; 1935), except for the extrapolation of the curve beyond N″ = 21. Deviations from the curve indicate that an oil is lighter (if above) or darker (if below) than the Lovibond glasses of the same N″ grade.

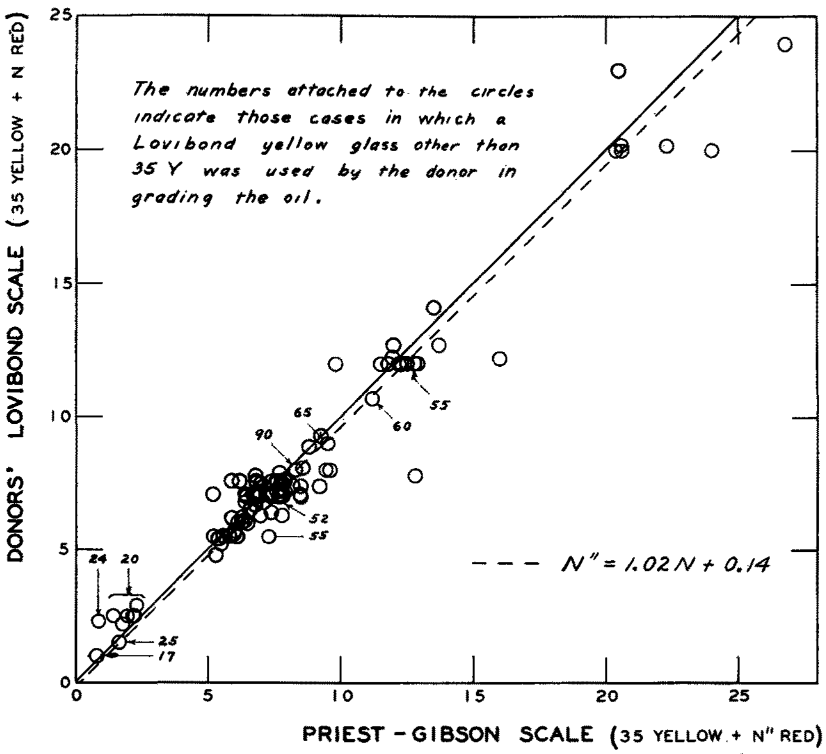

Fig. 2—This figure is the same as Fig. 9 of McNicholas's paper, except for the addition of the dashed line and equation. This illustrates that on the average the N" grade assigned an oil by the practical grader is the same as that obtained by the spectrophotometric method, but gives no indication as to whether the deviations may be correlated with excessively high or low transmittances of the oils.

consider is whether there is any significant correlation between the deviations of the points from the curves in Figs. 1 and 2; that is, whether the various horizontal deviations of the points from the dashed line of Fig. 2 may be correlated with the vertical deviations of the points from the curve in Fig. 1. This may be tested by plotting values of $(-\log_{10} 0.892\ T_s)_{actual} - (-\log_{10} 0.892\ T_s)_{curve}$ against values of $N''_{donor} - N''_{spectrophotometer}$. For this purpose only those values were used for which a 35-yellow glass was used, since, as already explained, the N" scale is defined in terms of a 35-yellow glass. Eighty-seven out of the 125 samples used by McNicholas met this condition and were available for the test.

The individual values were obtained as follows: Values of $N''_{spectrophotometer}$ were taken from column 8 of Table 1 of McNicholas's paper, values of N''_{donor} were obtained from the values of R (identical with N) in column 7 of that table by means of the relation $N'' = 1.02\ N + 0.14$, values of $(-\log_{10} 0.892\ T_s)_{actual}$ were derived from column 3 of the same

calibrated glasses bearing values of N (the N" scale not having yet been developed) one would not expect a perfect average agreement with values computed on the N" basis. Walker[7] has shown that on the average the relation between the values of N and N" is as follows:

$$N'' = 1.02\ N + 0.14.$$

Of course the ideal method of correcting the data would be to correct the plotted points by using the N" values for each of the donor's glasses. This would probably eliminate some of the larger discrepancies, in addition to effecting a better average agreement. Since this is impossible, the donors' grades having been assigned over 20 years ago, one might replot the graph, converting each value of N to N" by means of the above equation. An equivalent method, however, is to change the reference line from the continuous one with slope unity and intercept zero to the dashed line representing the above equation. This has therefore been done, and except for the few points of very low value it may be seen that this dashed line represents the points somewhat better than does the continuous line. This confirms the average relation between N and N" found by Walker.

The important question now to

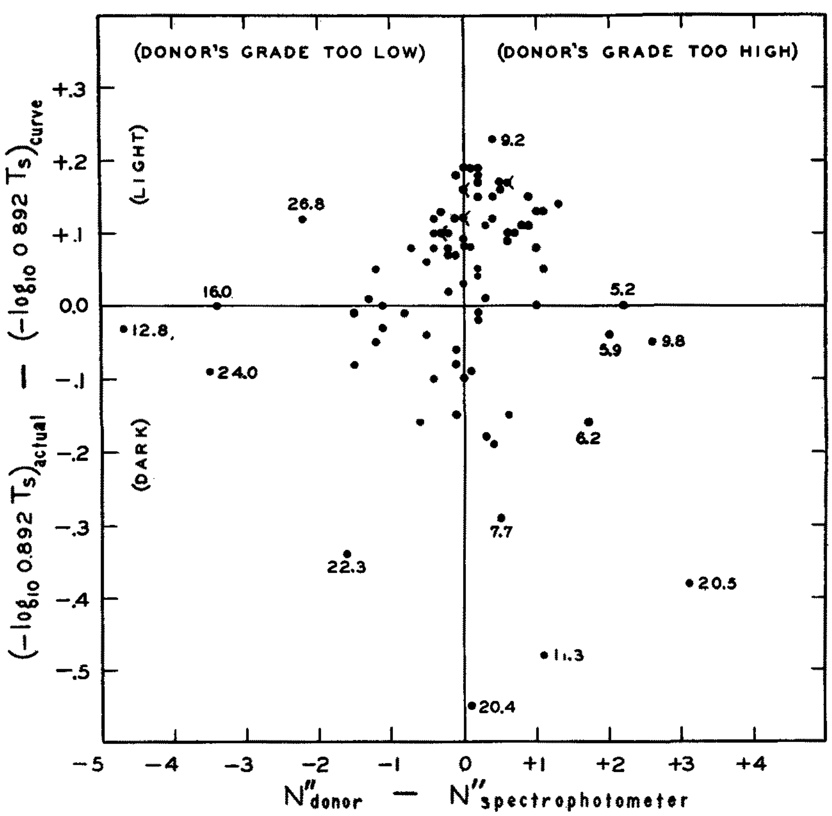

Fig. 3—Showing lack of correlation between (1) the lightness or darkness of an oil, and (2) the deviation of the donor's grade from the grade obtained by McNicholas from spectrophotometric analysis and colorimetric computations. The numbers refer to the N" values of the red glasses to which the particular points refer, these being given as a matter of interest for those points showing the greatest deviations.

table[8], and values of $(-\log_{10} 0.892\, T_s)_{curve}$ were read from the original large scale plot of Fig. 1.

The results are shown in Fig. 3. To assist in a ready understanding of this figure it may be noted that if the points plot above the horizontal line the oils are lighter than are the Lovibond 3-glass combinations having the same chromaticity; if below the line the oils are darker than the glasses. If the points are to the right of the vertical line the donor graded the oil too red, that is, he assigned a Lovibond red numeral higher than was obtained by the spectrophotometric method; if the points are to the left of this vertical line, he assigned too small a Lovibond red numeral to the oil.

If there were correlation between the two sets of differences the points should be distributed in either pair of diagonal quadrants. If, because an oil is light, the donor assigned it a Lovibond numeral that was too low, and correspondingly if he assigned too high a numeral because the oil was dark, then the points should be grouped in the upper left and lower right quadrants. If the converse were true, the points should be grouped in the other two quadrants. From the graph it is obvious that no such groupings exist, and it may be concluded at once without computing the coefficient of correlation that no significant correlation is to be found.

IV. CONCLUSIONS

It may therefore be concluded that the oil chemists have been justified in stating that the lightness or darkness of an oil is disregarded in giving the oil a Lovibond grade. However, this conclusion must be qualified in two respects: (1) It is based on data obtained about 20 years ago. It is possible, though hardly probable, that changes of personnel, instrument or technique would so affect the readings that a significant correlation might be obtained at the present time. (2) The lack of correlation shown is an average effect. It is not impossible that a single observer or laboratory would show a correlation of the type considered here.

However, the data presented in Fig. 3 would probably justify the oil chemists, in those cases where disputes arise, in accepting values of N″ obtained by the spectrophotometric method with no weight being given to the luminous transmittance of the oil. Many details would of course have to be considered before any such procedure could be put into effect. In particular the method would have to be enlarged to include evaluation of the oils in terms of Lovibond red and other than 35-yellow. Data are on file in the bureau by means of which such evaluation could be made if at any time it is seriously proposed to adopt this method of settling disputes.

REFERENCES

[1]McNicholas, H. J., The Color and Spectral Transmittance of Vegetable Oils, Oil and Soap **12**, 167 (1935); J. Research NBS **15**, 99 (1935); RP815.

[2]This observer and coordinate system are defined in terms of data published in 1922 in the Report of the Colorimetry Committee of the Optical Society of America (J. Opt. Soc. Am. and Rev. Sci. Inst. **6**, 527; 1922). Details of the computational procedure may be found by reference to the more recent bureau publications on Lovibond glasses and vegetable oils. Although a slightly different observer and a greatly different coordinate system are now in common use in colorimetry, known as the 1931 I. C. I. observer and coordinate system, the bureau's work on Lovibond glasses and vegetable oils will continue to be expressed in terms of the O.S.A. data for the sake of continuity with previous work. The values of N″ for either glasses or oils would not be importantly changed if recomputed by way of the I.C.I. data.

[3]See footnote 16 in McNicholas's paper.

[4]See, for example, Rules Governing Transactions between Members of the National Cotton Seed Products Association, Inc.; and Report of the (A. O. C. S.) Uniform Methods and Planning Committee, Oil and Soap **10**, 130 (July, 1933).

[5]See, for example, Geraldine K. Walker, Statistical Investigation of the Uniformity of Grades of 1,000 Lovibond Red Glasses, J. Research NBS **12**, 269 (1934); RP653. The complete list of bureau publications on Lovibond glasses and vegetable oils may be obtained from NBS Letter Circular LC-398, obtainable from the bureau on request.

[6]Kasson S. Gibson and Geraldine Walker Haupt, Standardization of Lovibond Red Glasses in Combination with Lovibond 35-yellow, Oil and Soap **11**, 246 (1934); J. Research NBS **13**, 433 (1934); RP718.

[7]RP653, p. 281.

[8]The sunlight transmittance of oil No. A 17 should be 0.050, instead of 0.504 as given in column 3 of the table; it is correctly plotted, however, in Fig. 8 (top).

NOTES ON THE DETERMINATION OF THE ALKALINITY OF SOAP SOLUTIONS

By WALTER C. PRESTON

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ALL who have attempted to study the alkalinity of soap solutions know that there are inherent difficulties in the procedure, and that while it is easy to get a reading to 0.1 pH unit, it is quite another thing to be sure that the reading tells the true story. Independent workers, both honest and capable, are more than likely to get divergent results when dealing with commercial soaps unless they use identical methods and apparatus in making their determinations, and there is wide difference of opinion as to what the best methods and the best apparatus are. Such solutions belong in the alkaline range, the range which is most difficult to study experimentally. They are sensitive to the action of CO_2. They are sometimes colored, usually more or less turbid, and frequently heterogeneous. Various mixtures of alkaline salts or "builders" are frequently present, while the soap itself is a mixture of the salts of various fatty acids, some saturated, some unsaturated, ranging from 10 to 18 or more carbon atoms. The equilibrium between neutral soap colloid, ionic micelle, and true crystalloid is slow of attainment; it is the same for no two of these soaps, and of course differs with change in temperature, dilution, etc. For these and other reasons, no current method of determining the hydroxyl ion concentration of these solutions can be considered truly satisfactory. Even the best of them have certain limitations that should be recognized. Whatever method is chosen, it is important that the difficulties to be met with, the uncertainties involved, the sources of error, and the probable accuracy of the final result be the subjects of careful consideration.

The Colorimetric Method

The colorimetric method is the oldest, the most widespread in use, and on its face apparently the easiest and quickest way in which to determine alkalinity. It does not necessarily follow, however, that it is the best, nor for that matter that in the long run it is the quickest or