closely as possible to the spectral transmission of the oils to be graded.

7. Some experimental work is described on the application of methods (1) and (2) to cottonseed oils. It was found, however, that the oils themselves were not sufficiently stable in color to serve as satisfactory color standards. Other possible standards were not investigated. Both methods were deemed unsuitable for routine commercial application, however, chiefly because of complications involving the independent variation in concentration of more than one important pigment in the oils. Each of these methods was designed to establish a practical one-dimensional chromaticity scale. Methods (3) and (4) provide the possibility of either one- or two-dimensional scales for all oils, but no experimental work has been done on the methods. They are suggested by the fundamental data presented in the paper.

# NOTE: CONCERNING THE EFFECT OF VARYING THE CONDITIONS OF THE AIR BLOWING ACCELERATED TEST FOR OILS AND FATS

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During our tenure of Industrial Research Fellowships at the Bureau of Chemistry and Soils of the U. S. Department of Agriculture, one of us[1] proposed a method of following the course of the oxidative deterioration of unsaturated oils and fats by means of an accelerated aging test. This method consisted of two parts: a. the accelerated "aging" process and b. the chemical determination of the extent of the oxidation. Since that time various workers have made critical studies and have proposed certain refinements in the procedure. These refinements have been mostly concerned with the first part, namely the accelerated "aging" or oxidation conditions. The most complete and detailed study of the aging conditions was made by King et al[2] in a recent paper in this Journal. These authors have carefully standardized the conditions of the accelerated aging by establishing certain very definite working limits. The most exacting of these limits was the rate of air flow used in blowing the samples. This entailed a very tedious and time-consuming calibration of several pieces of thermometer - capillary tubing, to give identical flow rates at any given pressure. Furthermore the flow rate which was used for this calibration was arbitrarily chosen as a purely empirical rate.

Shortly after the presentation[3] of the method proposed by Wheeler, it appeared more practicable to adopt a much lower air-flow rate for our subsequent work, namely, 4.8 liters per hour instead of the reported value of ten liters per hour. The subsequent appearance of the modified conditions specified by King and co-workers wherein another flow rate was used precluded the possibility of making a direct comparison of the data given in these papers. Furthermore, since King's paper contained valuable data resulting from a series of inter-laboratory compilations, it was deemed advisable to find a method whereby the various sets of data may be assembled.

A variable which has received little or no attention is the type or structure of the blowing jet used. It is obvious that the number of bubbles emitted by the same volume of air or flow-rate, would vary within wide limit depending upon the structure of the jet aperture or apertures. Wheeler (loc. cit.) specified the jet aperture empirically having no data at that time regarding the possible effect of a variance in this condition.

## Experimental

### *I. Effect of Rate of Air Flow During Aeration*

The apparatus used in these experiments was identical to that used by Wheeler (loc. cit.) at the Bureau of Chemistry, United States Department of Agriculture. However, a mechanical air pump was used here and the air humidified by bubbling through water. Also a bottle of acidified permanganate solution as shown by King et al, (loc. cit.) was included in the air line. The flow rate for each of the sixteen positions was measured by a calibrated flow meter, covering a range of 1-20 liters per hour at a pressure of two inches of mercury.

Reasoning from purely theoretical considerations we fully expected that the flow rate when varied over at least a two-fold range would affect the peroxide content of the oil or fat at any given point. First of all, it is generally held that the peroxide content is dependent upon at least two simultaneous actions, namely their formation and their decomposition. Taüfel and Seuss[4] indicate that oxygen itself may be split off or regenerated during the decomposition of the peroxides. This in addition to the keto-carbonyl products formed during the peroxide decompositions accounts for at least three simultaneous reactions all being presumably accelerated by the high temperature and the air blowing. Considerable evidence has accrued lately indicating that such active oxygen is regenerated as shown by the fact that the peroxide content accounts for only about half of the oxygen absorbed using a closed dynamic system.

Therefore with at least these three reactions involved it seems highly improbable that all three would be energized at exactly the same rate at widely varying air blowing rates. For example, if a

[1]Wheeler, Oil and Soap, 9, 89-97, (1932).
[2]King, Roschen and Irwin, Oil and Soap, 10, 105-9, (1933).
[3]Read before A. O. A. C. meeting at Chicago, November, 1931.
[4]K. Taüfel and A. Seuss, Fettchem. Umschau 6 (2), 107-113 (1934).

high blowing rate accelerated the peroxide formation and yet did not accelerate the decomposition rate *in proportion,* the peroxide values would be higher at a higher rate. The converse would obviously be equally true.

Additional evidence showing that these simultaneous reactions respond differently to different degrees of energization is given in the work of Coe and Le Clerc,[5] wherein light appears to be necessary for the decomposition of peroxides into the organoleptically obnoxious products. In other words the change in free energies accompanying the two reactions, the formation and the subsequent decomposition of peroxides is of a different order.

The following tables give in condensed form the results obtained by varying the rate of air blowing of three typical vegetable oils while maintaining the other conditions constant. Four flow rates were used to cover the most practicable range of use, namely 2.4, 4.8, 8.33 and 10 liters per hour. The latter two rates were selected as being identical with the rates used by King and Wheeler respectively.

TABLE I—CORN OIL

| Hours Blowing | 2.4 lit./hr. | 4.8 lit./hr. | 8.3 lit./hr. | 10 lit./hr. | % deviation from average |
|---|---|---|---|---|---|
| 2 | ... | ... | 7.3 | 7.8 | 3.2 |
| 2.25 | 6.9 | 5.7 | ... | ... | 9.5 |
| 3.5 | 14.4 | 16.5 | 12.5 | ... | 10.0 |
| 4 | ... | 20.7 | ... | 20.2 | 1.3 |
| 5 | ... | 25 | ... | ... | ... |
| 6 | 33.5 | ... | 33.8 | 36.0 | 2.2 |
| 7 | 42 | 38 | ... | ... | 5.0 |
| 8.5 | ... | 58 | ... | 53 | 4.5 |
| 9.25 | 60.5 | 63 | 63 | ... | 1.1 |
| Average per cent deviation | | | | | 4.6 |

TABLE II—SOYBEAN OIL

| Hours Aeration | 2.4 lit./hr. | 4.8 lit./hr. | 8.3 lit./hr. | 10 lit./hr. | % deviation from average |
|---|---|---|---|---|---|
| 1 | 1.9 | 1.4 | 1.5 | ... | 4.3 |
| 2 | 6.3 | ... | ... | 6.6 | 2.3 |
| 2.25 | 7.0 | 6.8 | 7.5 | 6.0 | 5.9 |
| 4 | 18.7 | ... | ... | 20.8 | 4.5 |
| 5 | 22.0 | 22.5 | 26.6 | ... | 1.4 |
| 6 | 30.9 | ... | ... | 33.7 | 4.2 |
| 7 | 35.2 | 38.7 | 43.6 | ... | 7.4 |
| 8.25 | 53 | ... | ... | 57.4 | 3.1 |
| 9.25 | 52.8 | 58.2 | 62 | ... | 5.5 |
| Average per cent deviation | | | | | 4.3 |

TABLE III—COTTONSEED OIL

| Hours Aeration | 2.4 lit./hr. | 4.8 lit./hr. | 8.3 lit./hr. | 10 lit./hr. | % deviation from average |
|---|---|---|---|---|---|
| 3.5 | 10.3 | 9.6 | 9.7 | 9.9 | 3.0 |
| 6.0 | 21.6 | 22.6 | 22.2 | 22.2 | 1.2 |
| 9.25 | 35.4 | 33.0 | 30.0 | 32.8 | 6.0 |
| Average per cent deviation | | | | | 3.4 |

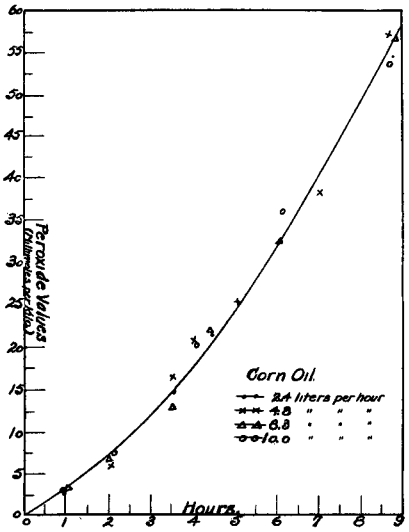
SUMMARY

Corn ... 4.6%
Soybean. 4.3%
Cotton... 3.4%
} Average = 4.1%

It appears from these tables that the mean variation for these three oils is about 5 per cent.

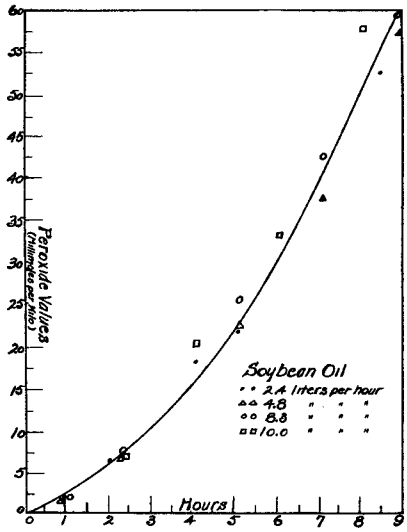
Using corn oil a set of duplicates were run at 8.33 liters per hour

[5]M. R. Coe and J. A. Le Clerc, Ind. Eng. Chem. **26**, 245, (1933).




during a nine hour period in an attempt to obtain the closest possible checks. The average deviation was found to be 3.3 per cent. This is the same order as that obtained using the five fold air flow variation, namely 4.1 per cent. The only general tendency noted was in the case of the highest flow rate wherein the values appeared to have a tendency to be lower than in the cases of the lower air flow rates. This may be due to the mechanical difficulties attendant upon high flow rates, especially if the fat is inclined to foam.

It is thus particularly fortunate that the above wide variation in the flow rate produces no detectable change in the rate of increase of the peroxide value. This observation therefore permits a direct correlation of the air blowing accelerated aging tests by various workers, provided the same temperatures have been used. It is noted at this point that the temperatures of the oil samples remained equal to that of




the heating bath at all four flow rates here employed. This indicates that no temperature error would be occasioned by the use of the varying flow rates given by individual workers.

*II. Effect of Type of Bubbling-Tube Orifice*

Five different types of tube orifices were constructed, being representative of the widest possible variations in design. The different types so constructed gave a wide variation in the sizes and numbers of air bubbles produced, which in turn varied the area of air-oil interface given per unit volume of air discharging from the different jets.

The five jets used were:

1. A capillary tube, 0.75 mm. inside diameter.
2. Macro-capillary, 1.00 mm. inside diameter.
3. Small glass tubing, 3-4 mm. inside diameter.
4. Sintered glass jet of medium filtration porosity.
5. Bell or funnel on end of small tubing giving 100 mm. inside diameter.

The sintered jet was of medium porosity, the granules passed 100 but caught on 125 mesh sieve. A fairly uniform cloud of small bubbles was produced in the oil at all flow rates. The bell jet produced large bubbles at a constant rate. These two jets represented the two extremes whereby the most and the least number of bubbles were produced. Since the reactions under study are assumed to be surface or interface reactions, this wide variance in the amount of air-oil interface area should demonstrate the magnitude of error possible by this variation.

TABLE IV—EFFECT OF TYPE OF JET

(Cottonseed Oil)

Peroxide Values (mmoles/kilo) using various types of jet (Jet numbers above)

IV a—Flow rate = 2.4 liters per hour

| Hours Aeration | 2 | 3 | 4 | 5 | Avg. Value | Per cent Deviation |
|---|---|---|---|---|---|---|
| 2 | 6.6 | 6.8 | 7.2 | 6.0 | 6.6 | 5.2 |
| 4 | 14.4 | 16.2 | 15.8 | 19.2 | 16.4 | 8.5 |
| 6 | 21.7 | 23.6 | 24.2 | 22.6 | 23.0 | 3.8 |
| 8.5 | 34.1 | 35.2 | 35.6 | 27.5 | 33.1 | 7.5 |
| Average deviation ..... | | | | | | 6.2 |

IV b—Flow rate = 8.3 liters per hour

| Hours Aeration | 1 | 2 | 3 | 5 | Avg. Value | Per cent Deviation |
|---|---|---|---|---|---|---|
| 3.5 | 9.7 | 9.5 | 9.7 | 10.6 | 9.9 | 4.0 |
| 6.0 | 19.0 | 22.0 | 22.0 | ... | 21.0 | 6.0 |
| 9.25 | 32.5 | 30.5 | 30.0 | 33.0 | 31.5 | 4.5 |
| Average deviation ..... | | | | | | 4.8 |

In consideration of the above results it appears that a very simple aeration tube consisting of conventional size glass tubing will serve the purpose. The important point in regard to the bubbling tube as well as the test tube container is

*cleanliness.* A relatively small number of bubbles per minute, just above counting rate, appears to give an adequate supply of oxygen as well as sufficient stirring.

### SUMMARY

The results of the experiments herein reported indicate that the rate of air flow used in aerating the oil samples under the conditions used, may be varied within wide limits, namely from 2.5 to 10 liters per hour, without impairing the range of accuracy inherent in the method.

The results of the experiments wherein the shape and type of jet orifice was varied over a greater range of sizes and types than is usually found in a laboratory set-up for aerating oils, show that this wide variance has no appreciable effect upon the accuracy of the method.

**(See Discussion of this paper in the July issue.)**

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## REPORT OF THE

# UNIFORM METHODS AND PLANNING COMMITTEE OF THE AMERICAN OIL CHEMISTS' SOCIETY

### MEMPHIS, MAY 24, 1935

THE Uniform Methods and Planning Committee has had several meetings in Memphis for the discussion of the various reports submitted, and the chairman is gratified that the full membership of his committee could be present.

*Seed Analysis Committee:*

The Committee on Analysis of cottonseed has studied the type of mill used for grinding and the determination of lint on seed. No changes are proposed but some progress has been made. The Uniform Methods and Planning Committee suggests that next year's committee continue the study of the methods which were undertaken during the present year.

*Free Fatty Acids Committee:*

The committee on free fatty acids states that the fifteen mesh screen previously recommended is unobtainable. It suggests the following changes:

(1) "Grind the meats in a Russwin No. 1 food chopper equipped with a sixteen tooth plate. Return the first few grams that pass the knives to the hopper to insure proper grinding."

The Uniform Methods Committee approves this change and moves its adoption.

The motion was properly seconded and the change accepted by the Society.

(2) Instead of specifying one and one-half hours on steam bath, change the method to read, "Allow to remain on steam bath until no trace of solvent remains."

The Uniform Methods Committee approves this change and moves its adoption.

The motion was properly seconded and the change accepted by the Society.

(3) Delete the use of 10cc. petroleum ether in the determination of free fatty acid.

The Uniform Methods Committee approves this change and moves its adoption.

The motion was properly seconded and the change accepted by the Society.

*Stability Committee:*

Owing to recent developments in the study of the technique of the peroxide method, the Uniform Methods Committee feels that the method as proposed should not be adopted as tentative at the present time, but should be remanded to the committee for further study.

*Moisture Committee:*

This committee has done interesting work on the study of various moisture ovens. The Uniform Methods Committee recommends to the incoming president that this committee be continued and be requested to continue the further study of various types of ovens.

*Color Committee:*

The Color Committee made the following recommendation for the reading of the color of crude cocoanut oil:

*"Crude Color:*

Melt the oil and filter through one thickness of approved filter paper at a temperature not above 35° C. until completely free from turbidity. Read the color using the following ratios of yellow to red:

| | |
|---|---|
| Up to 3.9 red | 6 Yellow to 1 Red |
| 4.0 to 4.9 red | 25 Yellow to 1 Red |
| 5.0 to 5.9 red | 30 Yellow to 1 Red |
| 6.0 to 6.9 red | 35 Yellow to 1 Red |
| 7.0 to 7.9 red | 40 Yellow to 1 Red |
| 8.0 to 10.9 red | 50 Yellow to 1 Red |
| 11.0 to 14.9 red | 70 Yellow to 1 Red |
| 15.0 to 19.9 red | 100 Yellow to 1 Red |
| 20.0 and above | 150 Yellow to 1 Red |

If the above ratios fail to give a satisfactory match, this fact should be noted and a second reading made, using the amount of yellow required for a good match. Report *both readings."*

The Uniform Methods Committee approves this change and moves its adoption.

The motion was properly seconded and the change accepted by the Society.

*Color Glass Development Committee:*

This committee has completed a very valuable piece of work. It has found a company which is willing to take our Lovibond glasses and grind them until they are exactly standard with the markings which appear on the glasses. The Uniform Methods Committee recommends and moves that referee chemists be requested to have the following red glasses prepared by the method described:

2.5
7.6
12
16
20