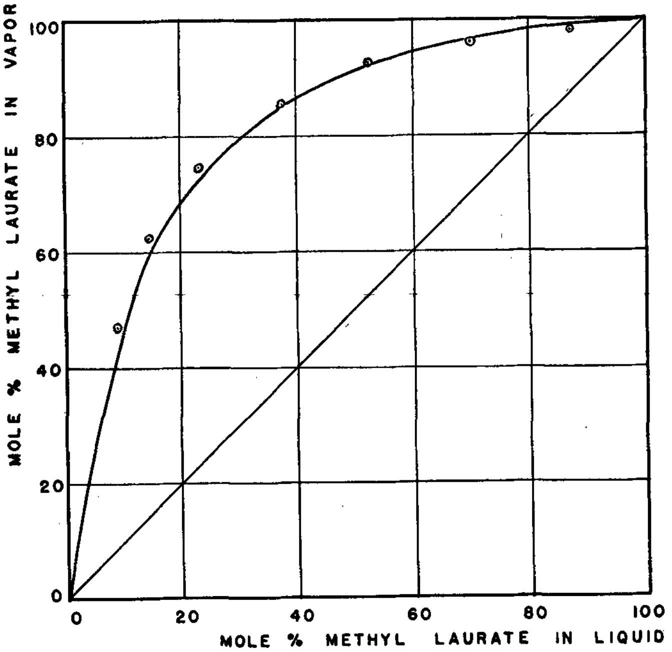


FIG. 6. Vapor composition vs. liquid composition for methyl laurate-lauric acid at 4 mm. pressure.
Circles, experimental data.
Solid line, calculated from Raoult's law.

ideal data. Deviation factors do not show any definite positive or negative trend from a value of 1.0, and the system can be said to obey Raoult's law at a pressure of 4.0 ± 0.2 mm. Hg.

Conclusions

The experimental vapor-liquid equilibrium data obtained with a mixture of methyl esters, and a mixture of a fatty acid and the corresponding methyl ester, were in agreement with calculated Raoult's law data at a pressure of 4.0 ± 0.2 mm. Hg.

The system lauric acid-myristic acid was observed to be non-ideal or not obeying Raoult's law at a pressure of 4.0 ± 0.2 mm. Hg. An average rate of polymer formation of 0.23% per hour at 155-170° C. was determined for mixtures of lauric acid and myristic acid.

The above work shows the feasibility of obtaining useful vapor-liquid equilibrium data for fatty materials at low pressures.

Acknowledgment

The authors are indebted to F. Schneider for the analytical work, to J. H. Percy and C. P. Arrowsmith for their valuable suggestions, and to J. Ross for supply of basic materials. They also wish to thank the Colgate-Palmolive-Peet Company for permission to publish this paper. The equilibrium still was constructed by the Scientific Glass Apparatus Company, Bloomfield, New Jersey.

BIBLIOGRAPHY

(1) Othmer, D. F., Ind. Eng. Chem., *35*, 614 (1943).
(2) Althouse, P. M., and Triebold, H. O., Ind. Eng. Chem., Anal. Ed., *16*, 605 (1944).
(3) Norris, F. A., and Terry, D. E., Oil and Soap, *22*, 41 (1945).
(4) Carlson, H. C., and Colburn, A. P., Ind. and Eng. Chem., *34*, 581 (1942).
(5) Pool, W. O., and Ralston, A. W., Ind. Eng. Chem., *34*, 1104 (1942).

Nomographs for Determining Relative Bleaching Costs of Adsorbents

R. B. LANGSTON and A. D. RICH
Filtrol Corporation, Los Angeles, Calif.

ONE of the problems confronting the refiner or chemist is to determine the relative merits of various bleaching adsorbents. It is frequently found, for example, that the more expensive absorbents are more economical to employ because their use effects a savings in handling costs and in lower loss of oil in the press cake.

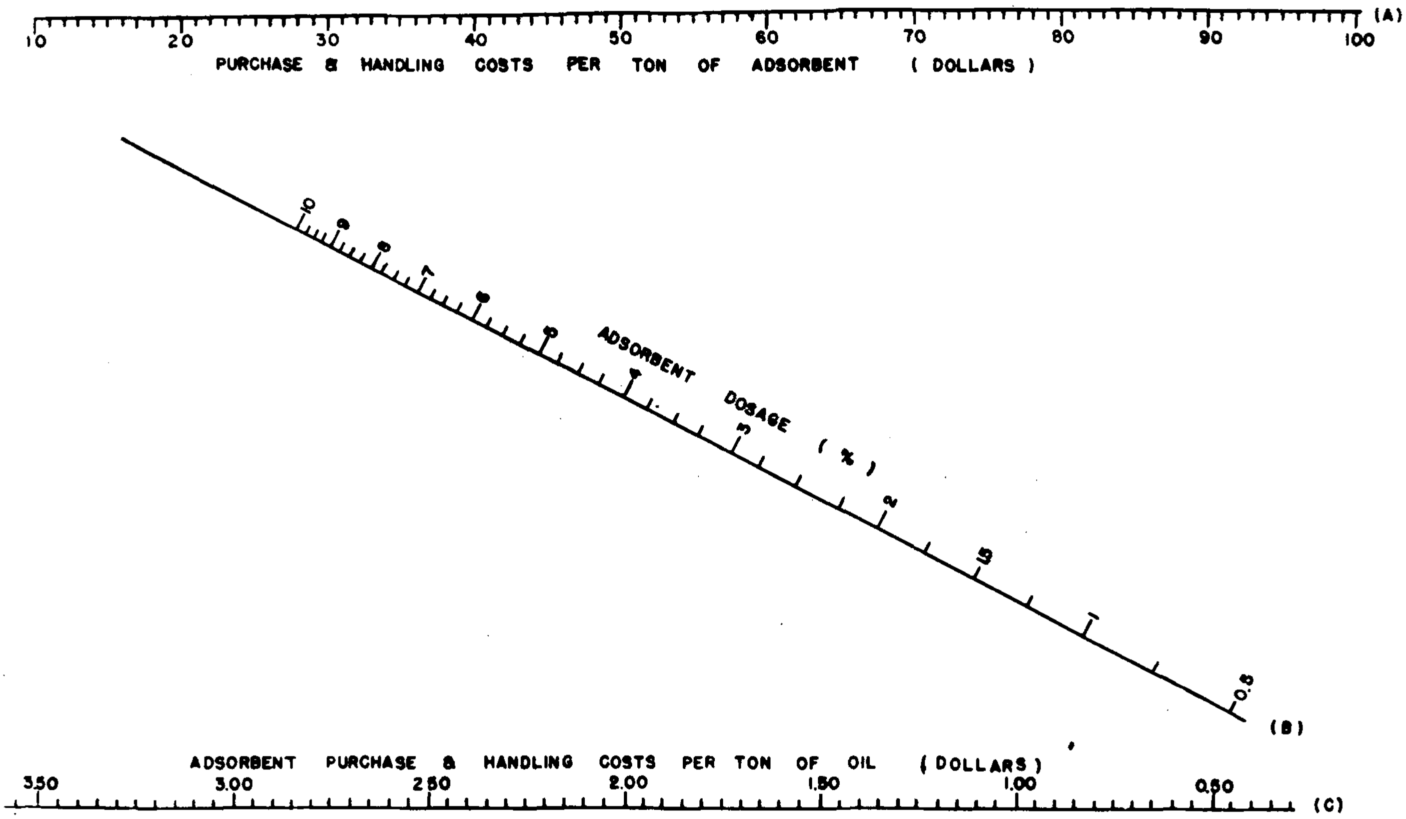
The accompanying monographs offer a rapid method for evaluating these differences between bleaching adsorbents. Two operations are involved: first, the determination of cost of adsorbent itself plus adsorbent handling cost, and second, the determination of value of oil lost in the press cake. The sum of these two items offers a basis for comparing adsorbents and is taken as the bleaching cost. Motive power and other costs incident to bleaching are assumed to be constant for all adsorbents. For convenience the computations are based upon bleaching one ton of oil.

The procedure is as follows:

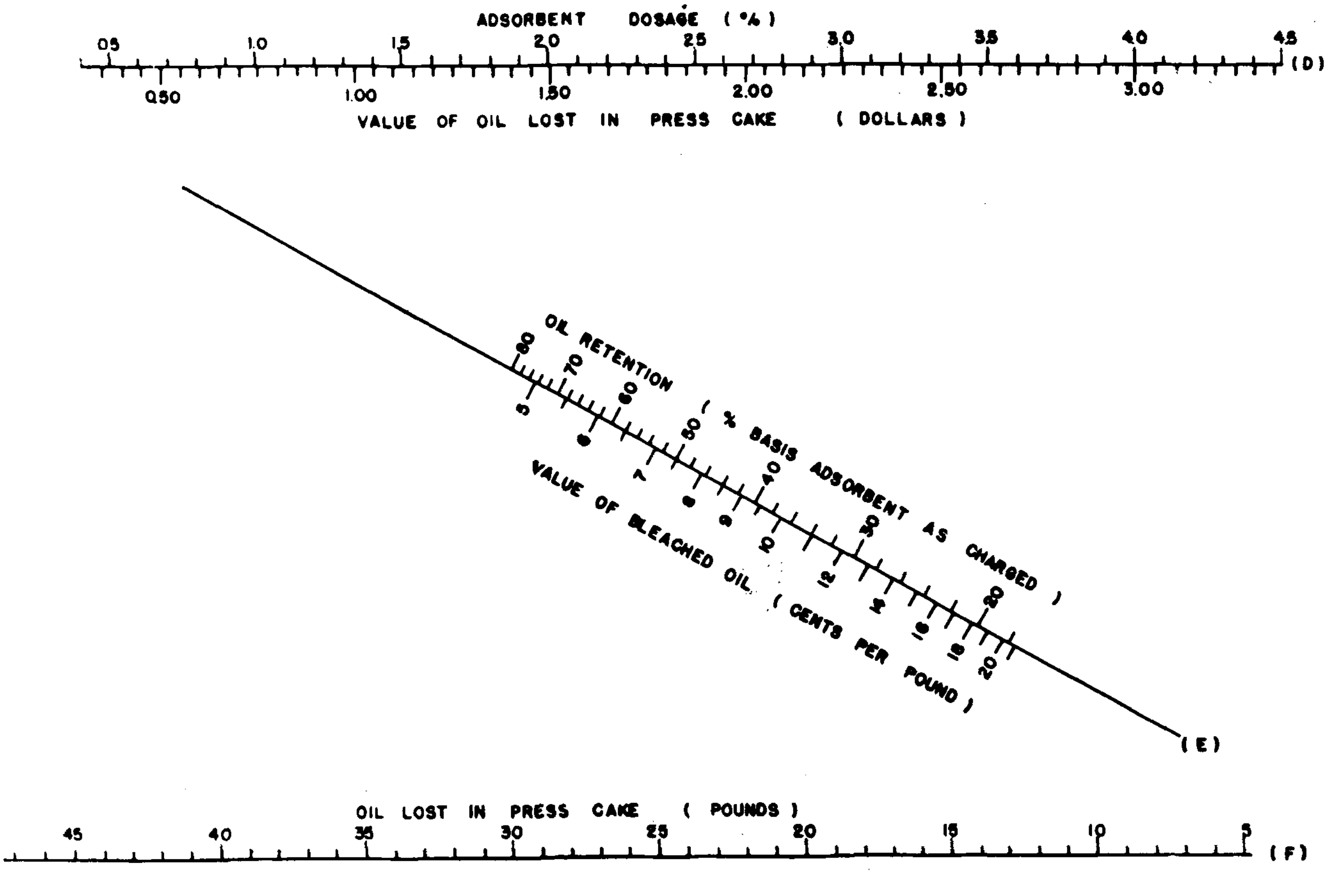
(1) *Cost of adsorbent itself plus adsorbent handling cost.*
Determine the cost of the adsorbent per ton as used. Add to this the cost of handling one ton of adsorbent. The example following illustrates how the cost of handling may be determined. Any plant can establish its own handling costs by substituting in the example its specific conditions.

(a) Unloading car — trucking to storage and stacking. (Requires 8 trips for one man, at $0.70 per hour, handling 5 bags at a time. Assuming 5 minutes per round trip, this would equal 40 minutes, or)	$0.47
(b) Trucking from storage to bleach tanks. (Requires 8 trips for one man, at $0.70 per hour, handling 5 bags at a time. Assuming 2 minutes per round trip, this would equal 16 minutes, or)	$0.18
(c) Opening bags and dumping into bleach tanks. (Requires one man, at $0.70 per hour, 20 minutes to open 40 bags and dump into tank at ½ minute per bag, or)	$0.23
(d) Dressing press. (Requires one man, at $0.70 per hour, one hour to dress a 1,000-pound press, or about 2 hours per ton of clay as charged)	$1.40
(e) Opening and cleaning press. (Requires one man, at $0.70 per hour, one hour to open and clean a 1,000-pound press, or about 2 hours per ton of clay as charged)	$1.40
(f) Trucking spent clay and bags away. (Requires 7 trips for one man, at $0.70 per hour, handling 400 pounds per trip. Assuming 5 minutes per trip and 2,800 pounds of used clay per ton of clay as charged, this would equal 35 minutes, or)	$0.41
(Total handling, 5.85 man-hours at $0.70 per hour = $4.09)	
(Assuming 10% of the sum of the above items for overhead, or)	$0.41
Total Clay Handling Cost per Ton of Clay as Charged	$4.50

NOMOGRAPH NO. 1



NOMOGRAPH NO. 2



Then, using Nomograph No. 1, extend a straight line from the "Purchase and Handling Cost per Ton of Adsorbent" (A-axis) through the "Adsorbent Dosage" (B-axis). The intersection with the C-axis gives the cost of adsorbent itself plus adsorbent handling cost based upon bleaching one ton of oil.

(Example: Cost of adsorbent as used is $52 per ton and cost of handling is $5 per ton. The sum is $57 per ton. Adsorbent dosage is 1.00%. Extending a line from $57 on the A-axis through 1.00% on the B-axis gives $0.57 as the cost of adsorbent plus handling to bleach a ton of oil.)

(2) *Value of oil lost in press cake.*

Determine the oil retention of the press cake as per cent of the adsorbent *as charged.* If the oil retention is calculated upon the basis of the spent cake (as is), or upon the basis of the spent cake (dry basis), employ whichever of the following formulae applies to convert the figure to the basis of adsorbent *as charged:*

(a) When oil retention is calculated on spent cake (as is basis), the oil retention basis adsorbent *as charged:*

$$= \frac{A(100\text{-}D)}{100\text{-}A\text{-}C}$$

(b) When oil retention is calculated on spent cake (on dry basis), the oil retention basis adsorbent *as charged:*

$$= \frac{B(100\text{-}D)}{100\text{-}B}$$

where
A = % oil retention of spent cake (on as is basis)
B = % oil retention of spent cake (on dry basis)
C = % moisture of spent cake
D = % moisture of adsorbent as charged

Then using Nomograph No. 2, connect a straight line from "Adsorbent Dosage" (upper side of D-axis) through "Oil Retention (Basis Adsorbent as Charged)" (upper side of E-axis). This line will intersect the F-axis to give the *pounds* of oil lost in the press cake.

Extend a line from this latter point *upwards* through the "Value of Bleached Oil" (lower side of E-axis). This will intersect the lower side of the D-axis to give the value of oil lost in the press cake.

[Example: Adsorbent dosage is 1.00%, oil retention (basis adsorbent as charged) is 35.0%, and value of bleached oil is 15c per pound. Extending a line from 1.00%, the adsorbent dosage on the upper side of the D-axis, through 35.0% oil retention (upper side of E-axis), intersects the F-axis at 7. This is the pounds of oil lost in the press cake in bleaching a ton of oil. Extending a line upward from 7 on the F-axis through 15c, the value of the bleached oil, intersects the lower side of D-axis at $1.05. This is the value of oil lost in the press cake in bleaching a ton of oil.]

The total cost of bleaching is taken as the sum of (1) the adsorbent and handling cost plus (2) the value of the oil lost in the press cake. (In the example, the total bleaching cost equals $0.57 plus $1.05, or $1.62 per ton of oil bleached.)

When the adsorbent dosage is greater than that covered by the scale of the nomograph, divide the adsorbent dosage by two and double the resulting adsorbent purchase and handling costs. Use the same method when calculating the value of the oil lost in the press cake. A similar procedure can be employed when the dosage is less than that covered by the scale.

Kinetics of Antioxygenesis[1]

CALVIN GOLUMBIC[2]
Biochemical Laboratory, State University of Iowa
Iowa City, Iowa

THE oxidative deterioration of natural fats and oils can be inhibited by certain phenolic and acidic substances. Mattill (1) recently proposed a tentative classification of such inhibitors into two broad groups, antioxidants and synergists. The antioxidants are phenolic compounds which have a primary antioxygenic action; the synergists are usually di- and poly-basic acids which reinforce the effect of the phenolic compounds instead of acting directly.

Upon exposure to air fats stabilized by antioxidants manifest a kind of behavior that is characteristic of chain reactions. There is a latent period, called the induction period, during which the absorption of oxygen and the accumulation of peroxides are slow, followed sometimes rather abruptly by a period of increasingly rapid oxidation. The induction period is generally attributed to a chain-breaking reaction between the activated fat peroxides (the carriers of the chain) and the inhibitors present.

Some idea of what may happen to antioxidants and synergists during the induction period has been gained from a series of kinetic studies on the oxidation of typical inhibitors in fat substrates (2, 3, 4, 5).

The first study (4) dealt with the oxidation of synthetic α-tocopherol in an animal fat substrate. It was found that tocopherol was rapidly oxidized throughout the course of the induction period of the fat substrate. Upon the complete disappearance of the tocopherol the induction period came to an end. At this point only about 30% of the initial tocopherol could be accounted for as tocoquinone. The further oxidation products have not been identified except in the case of γ-tocopherol (6), whose oxidation in fat substrates gives rise to a red chromane-5,6-quinone. This red ortho quinone had been isolated previously (8) from partially oxidized vegetable fats containing a native mixture of tocopherols and was found to possess some antioxygenic properties in contrast to tocoquinone, which has none.

During the induction period of a hydrogenated vegetable fat (4), the chromane-5,6-quinone formed rather gradually and subsequently disappeared at a more rapid rate. Its rate of oxidation, however, was relatively slow in comparison with that of tocopherol. This difference in oxidation rates between the two inhibitors offers a plausible explanation for the absence of a clearly defined induction period in vegetable fats. Organoleptic rancidity may appear in such substrates before there is a sudden increase in peroxide concentration. It was observed that peroxide formation continued at a slow rate even after the disappearance of tocopherol and did not rise abruptly until the concentration of chromane-5,6-quinone began to diminish. The successive action of the two inhibitors present thus appears to cause a retarda-

---

[1] Presented at the Conference on Problems Related to Fat Deterioration in Foods, under the auspices of the Committee on Food Research, Research and Development Branch, Military Planning Division, Office of the Quartermaster General in Washington, D. C., on June 21, 1945.

[2] Present address: Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania.