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:*

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

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

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

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]

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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-

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tion in the rate of peroxide formation even after the appearance of organoleptic rancidity.

Another factor requiring consideration is the concentration of tocopherol. It was found (4) that the rate of oxidation of α-tocopherol increased with progressive increase in its initial concentration. However, the time necessary for the oxidation of any given fraction of tocopherol was independent of its initial concentration. There is an optimum concentration where tocopherol exerts its maximum antioxygenic activity. It is thus of little value for the stabilization of vegetable fats whose natural tocopherol content is already high.

TABLE I

The Oxidation of α-Tocopherol in the Ethyl Esters of Lard Fatty Acids, in the Presence and Absence of Ascorbic Acid (2)

Amount of α-Tocopherol in 1 g. of Ester [a]

Time, hours	(No ascorbic acid)	(0.05 per cent ascorbic acid)	(0.10 per cent ascorbic acid)
0	1000	1000	1000
3		540	482
5	66		
10	trace		
20	0	313	336
44		120	164
66		0	35
70			0
Length of induction period,[b] hours	11	59	68

[a] Determined by the method of Emmerie and Engel (20).
[b] Determined by the oxygen absorption method, at 75° C.

Possibly this relationship between antioxygenic activity and concentration of tocopherol holds for other phenolic inhibitors as well. If this is indeed the case, the stability of a fat containing the optimum amount of one antioxidant will not be augmented appreciably by further additions of the same antioxidant and possibly not even by the addition of a closely related inhibitor. This may perhaps be the reason for the relative ineffectiveness of hydroquinone in vegetable fats (12).

Such fats can, however, be stabilized by the addition of appropriate synergists, usually di- and polybasic organic and inorganic acids. The results given in Table I disclose the manner in which these acid synergists function. The rate of disappearance of α-tocopherol in an animal fat substrate is retarded in the presence of ascorbic acid. With equal amounts of tocopherol initially present increasing amounts of ascorbic acid progressively diminish the rate of tocopherol oxidation and thereby lengthen the induction period. At the termination of the induction period, in each instance, the tocopherol is completely oxidized. Ascorbic acid is also oxidized by the fat substrate but at a much slower rate than tocopherol. The oxidation of ascorbic acid is catalyzed by tocopherol as was shown in the ascorbic acid-quinone-lard esters system investigated by Calkins and Mattill (5). These workers measured the absolute reaction rate of oxidation of ascorbic acid in lard esters both in the presence and absence of quinone. The free energies of formation of the activated states were calculated for each case. It was found that the addition of quinone lowered the free energy level sufficiently to allow the ascorbic acid to be oxidized rapidly. The quinone acted as a catalyst in this process because at any time during the induction period the original amount could be quantitatively recovered.

The present tentative explanation for these observations is that the antioxidant is being regenerated continually at the expense of the synergist. This mechanism implies that the oxidation of the antioxidant is in part reversible. According to Conant (13) and Fieser (14), the oxidation of phenolic substances proceeds in two stages; the initial step is reversible and consists of the production of a phenoxyl radical which forms an unstable oxidation-reduction system with the phenol. In the case of quinols, as shown by Michaelis (15), the first step is the formation of a semiquinone and it is followed by a second reversible step to give a quinone. In the proposed synergistic mechanism the assumption is made of an oxidation-reduction reaction between the synergist and an oxidized form (phenoxyl, semiquinone,quinone) of the antioxidant whereby the latter is maintained in the reduced state as long as there is synergist available to furnish hydrogen. In effect, the synergist acts as a reservoir of hydrogen which is transferred by way of an intermediary redox system, the antioxidant, to the activated fat peroxide. The final step in the process, the reduction and deactivation of the energy-rich peroxide, breaks the reaction chain of autoxidation.

There seem to be two major prerequisites for this synergistic mechanism. First, a difference in oxidation potential must exist between the antioxidant and synergist; and second, the relative speeds of the reactions involved in the process must be such that the oxidation of the synergist by the oxidized form of the antioxidant is faster than the oxidation of the

TABLE II

Relation of Antioxygenic Activity and Oxidation Potential

Compound	E [a] mv.	E [b] mv.	Antioxygenic Index [c] of Reductant in Lard at 75°
Phenol	1089		1
m-Cresol	1080		1
2-Phenanthrol	1057		1.5
Resorcinol	1043		1
o-Cresol	1040		1
p-Cresol	1038		1
β-naphthol	1036		2
3-Phenanthrol	1013		2
1-Phenanthrol	848		15
Phloroglucinol	799		3
9-Phenanthrol	798		6
α-Naphthol	797		22
Naphthoresorcinol	752		5
Gallic acid		799	18
Catechol	742	793	41
1,5-Dihydroxynaphthalene	673		36
Hydroquinone	631	714	38
Pyrogallol	609	713	60
Toluhydroquinone		656	7
Hydroxy hydroquinone		601	60
α-Tocopherol	770 [e]	656-597 [d]	3
2,5-Dimethylhydroquinone		597	3
Naphthotocopherol		(573) [f]	6
Chromane-5,6-quinone (from tocopherol)		541 [g]	2-4
Trimethylhydroquinone		526	1
Dehydro-iso-β-lapachone [h, i]			3
1,4-Naphthohydroquinone		484	2
Durohydroquinone		466	1
2-Methyl-1,4-naphthohydroquinone		408	1.5
β-Lapachone [h]		403	1.5
Ascorbic acid		390	1
Vitamin K_1		363	1
α-Lapachone [h]		304	1
Lomatriol [h]		300	1
Lapachol [h]		800	1
2-Methyl-3-hydroxy-1,4-naphthohydroquinone		299	1

[a] Critical oxidation potential (14).
[b] Normal oxidation potential (19).
[c] Ratio of induction period of stabilized fat to that of control. It represents the average of several tests at 0.02 per cent inhibitor concentration.
[d] Apparent oxidation potential (17).
[e] Extrapolated value (11), for normal oxidation potential.
[f] This is an extrapolated value for a lower homologue (16).
[g] Approximate extrapolated value (18).
[h] Samples of these compounds were generously furnished by Dr. L. F. Fieser, of Harvard University.
[i] Tentative position assigned on basis of preliminary experiments.

antioxidant by the fat peroxides which in turn is faster than the oxidation of the synergist by the fat peroxides.

It seemed worthwhile to examine the possibility that combinations fulfilling only the requirements as to potential would show synergistic activity. The first step taken in this direction was to compare the oxidation potentials and antioxygenic activities of a large number of phenolic compounds. In Table II, the phenolic compounds are arranged according to decreasing oxidation potentials. These values, compiled from the literature, are measurements made in aqueous or aqueous alcoholic solution. The oxidation potentials in fat systems are unknown. It may well be that in non-aqueous systems, such as fats, the positions of the individual phenolic compounds in the potential series remain relatively unchanged. This is the trend that may be noted in the data of Kvalnes (19) who measured oxidation potentials in benzene solution.

The antioxygenic indices given in Table II were determined at the University of Iowa by an oxygen absorption method. It will be noted that the most effective fat antioxidants are found in the potential region between 848 and 484 millivolts; above and below these limits the antioxygenic activity is small or entirely lacking.

Many pairs of compounds in this series were examined for synergistic activity; in each of the combinations the component of higher oxidation potential always fell within the range of effective inhibitors. Many interesting synergistic combinations were discovered among them (7). Typical examples are given in Table III. The first example is of two phenolic inhibitors, α-tocopherol and 1,4-naphthohydroquinone, which when used together manifest a synergistic effect. To distinguish between the antioxidant and synergist in such a combination the compound of lower oxidation potential, in this case 1,4-naphthohydroquinone, may be called the synergist. When the naphthohydroquinone was replaced by the corresponding naphthoquinone, the result was only additive. The synergism failed presumably because of a coupled reaction between the inhibitors was not possible. A number of such combinations, incapable of redox reaction, were tested and found to be devoid of synergistic activity.

TABLE III

Synergistic Combinations in Lard

No.	Per cent Inhibitor Added	Antioxygenic Index[a] at 75° C.
1.	0.02 α-Tocopherol	2
	0.02 1,4-Naphthohydroquinone	1.5
	Combination	7[b]
2.	0.02 α-Tocopherol	2
	0.10 2-Methyl-1,4-naphthohydroquinone	1.3
	Combination	6.5[b]
3.	0.10 Chromane-5,6-quinone	17
	0.10 2-Methyl-1,4-naphthohydroquinone	3.3
	Combination	28[b]
4.	0.02 Toluquinone	41
	0.02 α-Tocopherol	1.5
	Combination	84
5.	0.01 Gallic acid	1.3
	0.04 Tocopherol (concentrate)	2
	Combination	5.3[b]
6.	0.04 Naphthotocopherol	5.8
	0.10 Ascorbic acid	1
	Combination	8.2

[a] Ratio of induction period of stabilized fat to that of control.
[b] Fresh when discontinued.

The second synergistic pair given in Table III is noteworthy because it represents a combination of antisterility and antihemorrhagic compounds. A synergistic effect was also observed when a mixture of 2-methyl-1,4-naphthohydroquinone and ascorbic acid was used in a vegetable fat. In this case the synergism represents an interaction between compounds having the biological activities of vitamins C, K, and E.

The third and fourth examples are instances in which the antioxidant, the component of higher oxidation potential, is initially in its oxidized form. In the fourth and fifth examples, the synergist is tocopherol, a compound ordinarily thought of only as an antioxidant. The last example, naphthotocopherol, is of interest because it is intermediate in structure between vitamins E and K. Its antioxygenic activity is about equal to that of β-tocopherol. Recent work has shown that many other synthetic chromans, coumarans, and naphthohydroquinones related to vitamins E and K are effective stabilizers (9, 10).

Mixtures of homologous hydroquinones and tocopherols did not exhibit any synergistic action; doubtless there will be many more such exceptions until the mechanism of this kind of synergism is more firmly established.

The synergism of another group of compounds, the organic di- and poly-basic acids, may be similar fundamentally to that described above, but as yet no definitive mechanism for them has been proposed. A start has been made in the case of the inorganic acid synergist, phosphoric acid. It was found that through the agency of this acid the fat substrate alone may serve as a hydrogen donator for the reduction of the oxidized form of the antioxidant. Thus benzoquinone and also α-tocoquinone become powerful stabilizers in its presence, indicating that they are reduced to hydroquinone and α-tocopherol, respectively (3). The presence of regenerated tocopherol in the latter instance was confirmed by biological assay for vitamin E.

It is evident that the subject of synergism is a very broad one and still in its formative stages, but enough work has been done to show that it offers many opportunities of theoretical and practical interest.

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