Anti-oxidants in Edible Oil Preservation *

Resistance to Oxidation Attributable to Presence of Minute Quantities of Added or Natural Inhibitory Catalysts

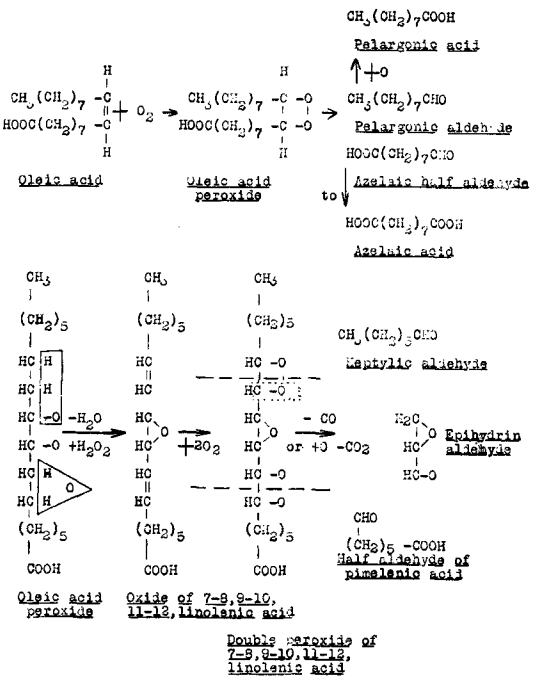
By F. C. VIBRANS

Part II

AN adequate review of Powick's research, although it would be very much worthwhile, cannot be undertaken at this time. From his study he concludes that "the odor of heptylic aldehyde ($C_6H_{13}CHO$) itself and in the presence of fresh fats is sufficiently suggestive of the rancid odor to establish the reasonableness of Scala's[13] contention that it is the component of rancid fats that is primarily responsible for their rancid odor." Powick, after an examination of nonylic aldehyde, suggests that this compound may be partly responsible for the rancid odor. He found the color obtained in the Kreis test on rancid fats was identical spectroscopically with that obtained in the Kreis test on mixtures of acrolein and hydrogen peroxide. The product formed was identified as epihydrin aldehyde $H_2=C+C+CHO$ (with O bridging the two C's). Because of its instability it could not be isolated, but its diethylacetal (CH_2 + CH + O) $CH(OC_2H_5)_2$ was synthesized. Powick does not think that the substance in rancid fat that gives the Kreis test is epihydrine aldehyde, but that epihydrine aldehyde is formed when the fat which gives a Kreis test is shaken up with concentrated hydrochloric acid.

To illustrate how Powick juggles the oxidation of oleic acid to get the compounds which have a rancid odor and give a positive Kreis test, I have prepared this chart.

Powick, Kerr and Sorber, Eibner and Palouf[23], Tschirch[24], Holm, Greenbank and Deysher[25], and others have contributed to the chemistry of the oxidation of fats and oils. Whether they explained the oxidation process by assuming the formation of a peroxide or a peroxide like compound which some of them call an ozonide or a "moloxide," the suggested mechanisms are all more or less alike.



Oxidation of Oleic Acid (Powick)

The oxidation of fats and oils takes place in two stages. The first stage, called the inductive period, may be either short or long, depending on a number of factors, and during which the compounds of high oxidizing potential are accumulating in sufficient amount to start a more rapid oxidation. The second stage is one of rapid oxidation. In this second period the retarding effect of anti-oxidants has been overcome and oxidation proceeds unmolested.

There is considerable evidence to support the belief that fats and oils contain anti-oxidants, or else they take up pro-oxidants, from apparently no apparent source. It is well known that raw cottonseed oil keeps bet-

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ter than the refined product. Of course this may be attributed to the refining process per se. but there is evidence available to support the belief that the refined oil keeps more poorly because of the removal during the refining process of an anti-oxidant. Mattill and Crawford[26] studied the keeping quality of raw extracted, raw expressed, and processed corn oil. Their data indicate that the petroleum ether extracted oil kept many times better than a corresponding raw expressed oil, which necessarily was heated hotter during processing than the extracted oil. The maximum temperature of the extracted oil was 50° C. The processed oils kept poorer than the raw oil from which they were prepared. More references of this nature might be cited, but sufficient have been presented to indicate that unprocessed fats and oils evidently contain anti-oxidants to protect them from atmospheric oxidation.

Experimental Data

TO determine the effect of known anti-oxidants on the keeping quality of lard, we have tested a number of them in our laboratory. The method we use is a modification of a method developed by Greenbank and Holm of the Bureau of Dairy Industry in Washington. It consists essentially of measuring with an automatic recording device the time in hours required for 10 cc. of fat contained in a specially designed flask when heated at a constant temperature of 90° C. to absorb 3 cc. of oxygen from the air contained in the flask. The following are a few of the data we have obtained in our laboratory and I present them to you to illustrate how the use of anti-oxidants may improve keeping quality of edible fats.

Sample	Antioxidant Added		O_2 Absorption
No. 12	None		14.5
" "	0.01	Agerite	21.4
" "	0.2	"	109.
" "	0.5	"	123.
" "	1.0	"	94.
No. 12	None		14.5
" "	0.01	Thymol	17.
" "	0.05	"	19.
" "	0.10	"	23.
" "	0.20	"	28.
" "	0.50	"	25.
" "	1.00	"	24.
No. 11	None		10.4
" "	0.01	Everite	16.4
" "	0.05	"	20.1
" "	0.10	"	32.
" "	0.20	"	40.
" "	0.50	"	40.
No. 32	None		13.1
" "	0.2	No. 1	24.
" "	0.2	No. 2	19.
" "	0.2	No. 4	63.
No. 35	None		5.7
" "	0.01	No. 5	7.6
" "	0.20	" "	10.1
" "	0.01	No. 7	9.9
" "	0.20	" "	19.8

The difficulty in finding an anti-oxidant that can be added to edible fats and oils lies in the fact that before such a compound can be used, it must be not only fat soluble, but it must be non-toxic, odorless, tasteless, colorless, and on standing or on heating, must not darken in the fat. When a suitable anti-oxidant is found, it will have wide use because the fat spoilage problem is always present.

In the field of mineral oils, where the products are not for human consumption, anti-oxidants are used to prevent deterioration. According to Hyman and Wagner[27], cracked gasolines on standing, especially if they are exposed to light, develop a gum in them. Experiments have shown that gum formation in cracked gasoline is inhibited by the addition of a small amount of a gasoline soluble dye. This may possibly be a partial explanation of why there are so many different colored gasolines for sale at the different filling stations, but more likely these dyes have been added for sales reasons.

There have been patents taken out for the use of anti-oxidants in transformer oils. One of these called "ohmail" has had the rubber anti-oxidant age-rite (phenyl-alpha-napthylamine) added to it. Just how largely anti-oxidants are used in transformer oils, I cannot say, but evidently not very extensively, because in a communication received from one of the large users of transformer oils, they state; "The difficulties encountered, however, in oil is that most of these anti-oxidants volatilize from the oil at elevated temperatures, or else precipitate as a sludge as oxidation proceeds. The remedy, of course, in the latter case is as bad as the original disease."

A research director for a manufacturer of gasoline and oils, including transformer oils, informed me not very long ago that as far as he knew anti-oxidants are not used to any extent in either cracked gasoline or transformer oil.

No discussion of anti-oxidants would be complete without mention of their use in the rubber industry. Although they were first developed for use in the manufacture of rubber tires for automobiles, they are now used in practically all manufactured rubber goods. There is quite a long list of compounds that are used to inhibit the oxidation of rubber. Among these compounds that now may be bought on the general market are: "V.G.B." Acetaldehyde-

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Anti-Oxidants

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ethylene-diamine, "Stabilite" Diphenyl-ethylene-diamine, "Age-Rite" Phenyl-alpha-naphthylamine, "Neozone" Phenyl-Beta-Naphthylamine, "Antox" Butylaldehyde-aniline.

An interesting observation on the action of anti-oxidants in rubber was reported by P. C. Jones and David Craig a few months ago at the American Chemical Society meeting in Cincinnati. They reported that with anti-oxidants of the secondary aromatic amine type, maximum effectiveness was reached upon the addition of one percent of the anti-oxidant. With anti-oxidants of the aldehyde-type, the limit is not one percent, it may be as high as 6, 7, or even a higher percent of the anti-oxidant. We had noticed in our work that when varying amounts of age-rite and thymol were added to lard, concentrations were reached above which the anti-oxygenic property of these compounds no longer increased with increased amounts of anti-oxidants. On the other hand, large amounts of age-rite, one percent or more, had less anti-oxygenic action than two-tenths percent. The maximum effect was produced when approximately 0.5% of age-rite, or 2% thymol was used.

In conclusion, may I hope that by this more or less general discussion in which I tried to give you something of the history, the theory and the practical value of anti-oxidants, I have stimulated your interest in them as a means of preserving edible fats and oils.

REFERENCES

1. Berthollet, (Jour. de l'Ecole polytechn., series 3, 277 [1797]).
2. Davey, Trans. Royal Soc. London, 1817, 45; Ann. Chem. phys. (2) 4, 347 (1817).
3. Deschamps, J. Pharm. Chim. (3) 4, 201, (1843).
4. Frankland, Chem. News. 6, 3 (1862).
5. Rump, Ueber die Prufung des Chloroforms, Hanover (1868).
6. Bigelow, Z. phys. chem. 26, 493 (1898).
7. Welborn, Pharm. J. 83, 390 (1909).
8. Siebeneck, Petroleum 18, 281 (1922).
9. Titoff, Zeit. phys. chem. 45, 641 (1903).
10. Alyea and Bäckström, Jour. Amer. Chem. Soc. 51, 90 (1929).
11. Moureu and Dufraisse, Chemical Reviews 3, 113 (1926-27).
12. Harris, Ber. 38, 1630.
    39, 3228.
13. Scala, Gaz. Chim. Ital., 38 (1) 307.
14. Canzoneri and Bianchini, Ann. Chim. Applicata 1, 24.
15. Langbein (j. prakt. Chem. 41, 1890).
16. Nicholet & Liddle, Ind. Eng. Chem. 8, 416 (1916).
17. Salkowski, Genussm 34, 305.
18. Stärkle, Biochem. Z. 151, 371 (1924).
19. Browne, Jour. Amer. Chem. Soc. 21, 975.
20. Watker, Philippine Jour. Sci. 1, 117.
21. Kerr & Sorber, Ind. Eng. Chem. 15, 383.
22. Powick, Jour. of Agricultural Research XXVI., 323, 1923.
23. Eibner and Pallouf, Chem. Umschau, 32, 81, 97 (1925).
24. Tschirch, Chem. Umschau. 32, 29 (1925).
25. Holm, Greenbank and Deysher, Ind. Eng. Chem. 19, 156 (1927).
26. Mattill and Crawford, Ind. Eng. Chem. 22, 341, (1930).
27. Hyman and Wagner (paper before the petroleum section of the A. C. S. in Cincinnati, 1930.)

The Port Gibson Oil Works, of Port Gibson, Mississippi, has filed a complaint with the Interstate Commerce Commission attacking freight rates on cottonseed from Louisiana and Arkansas points to Port Gibson. The complaint declares that the rates are higher, distance considered, than the rates prevailing in Louisiana and Arkansas.

The Matson liner *Sonoma* docked recently at San Francisco with fire in cargo holds containing copra. The vessel had just completed a trip to the Antipodes, returning via Suva and Pago Pago, where a good cargo of copra was loaded. The blaze is said to have caused several thousand dollars damage before it was extinguished.

Bureau of Entomology of the U. S. Department of Agriculture has announced the appointment of R. W. Harned as leader of its division of cotton insect investigations, effective June 20. He succeeds B. R. Coad, resigned. Mr. Harned is head of the Mississippi State plant board, and since 1908 has been professor of Zoology and entomology at Mississippi A. & M. College.

Mexican Tariff Increases

A Mexican Presidential decree, now effective, materially increases the rates of import duty on various commodities including pork lard and lard compounds, oleomargarine, animal and vegetable oils and fats, and certain oil seeds. The new rates of duty in Mexican pesos are as follows, old rates also being shown:

Food Products	*New Rate*	*Old Rate*
Pork lard in tank cars (per net kilo)	0.20	0.10
Pork lard in other containers (gross kilo)	0.30	0.15
Lard compounds and substitutes (gross kilo)	0.40	0.20
Oleomargarine (per legal kilo)	0.80	0.60
Animal and Vegetable Oils and Fats		
Cottonseed and sesame seed in tank cars or tank vessels (per net kilo)	0.20	0.10
Cottonseed and sesame seed weighing with the immediate container more than 50 kilos (per gross kilo)	0.25	0.12
Animal and vegetable oils, not specified, in tank cars or tank vessels (per net kilo)	0.20	0.10
Animal and vegetable oils, not specified, weighing with the immediate container up to 50 kilos (per gross kilo)	0.40	0.30
Animal and vegetable oils, not specified, weighing with the immediate container more than 50 kilos (per gross kilo)	0.25	0.12
Edible vegetable fats, solid at a temperature of 20 degrees Centigrade, substitutes for lard compounds (per gross kilo)	0.40	0.20
Animal and vegetable fats and greases not specified, weighing with the immediate container up to 50 kilos (gross kilo)	0.40	0.20
Animal and vegetable fats and greases not specified, weighing with the immediate container more than 50 kilos (gross kilo)	0.25	0.10
Cottonseed (per gross kilo)	0.03	0.008
Sesame Seed (per gross kilo)	0.10	0.04