The upper curve shows the detergent values obtained when the soap concentration was maintained at 0.3% and the tallow soap was removed and replaced with the indicated proportions of sodium resinate of hydrogenated rosin. The distance between the upper and lower curves represents the amount of detergency that the resinate contributed to that of the whole mixture. Only the curve for hydrogenated rosin is shown since it is typical of all those obtained using the several types of modified rosins tested. Since sodium resinate, like sodium laurate, is not a very good detergent at the concentration of 0.3%, we believe that the reason for its maintaining the detergency of the fatty acid soaps, as shown in Figure 4, is due to the increase in the wetting power which was discussed in the preceding paragraphs.

We also have indications that the addition of sodium resinates increases the emulsifying power of soap, but since there is no standard method for the determination of this property, no specific data along this line are presented. This property may, however, contribute something to the detergency of fatty acid soap—resinate mixtures.

In general, the effects of temperature, pH, and the several alkaline builders on soap products containing the modified rosins was found to be the same as for straight fatty acid soaps. These effects are so well known that it is unnecessary to go into more detail in the present paper. The use of modified rosins is not limited to any one type of soap. They have been used in milled toilet soap, floating soap, chip soap, and granulated or spray-dried soaps and have proven entirely satisfactory in every case.

Summary

We have endeavored to show the advantages that rosins modified by hydrogenation, dehydrogenation, or polymerization have over ordinary rosins when used in soap.

Ordinary rosin darkens in color upon oxidation. The modified rosins are not as susceptible to oxidation, and, therefore, soaps made using them do not darken in color to any greater extent than is normal for a soap made from the same fat stock but without rosin.

The modified rosins when used as a replacement for part of the fat in soap making increase the rate of solubility of soap to a greater extent than do the ordinary rosins. They also show a slight advantage on the amount and stability of the lather.

Hydrogenated rosin should be considered wherever germicidal value is desired since it contains a large proportion of tetra- and di-hydroabietic acids which have been shown by other investigators to have greater germicidal activity than the ordinary rosin acids or the fatty acids.

The addition of modified rosins increase the wetting action of fatty acid soaps.

It is indicated that up to 50% of modified rosin can be added to soap without decreasing detergent action, which, taken together with its other beneficial properties, makes it an ideal extender for fatty soap stocks.

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Oxidative Deterioration of Fats in Cereal Products*

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THE PROBLEM of fat deterioration in cereal products presents more complications than a similar deterioration of commercial fats. The possible effect of each component of the cereal product on fat deterioration must be considered. So also must the various procedures involved in the processing of the product, such as mixing, baking, etc., as well as the packaging. Let us consider briefly each of these factors in their relation to fat deterioration.

Shortening Agents. Practically all baked goods as well as prepared mixes contain in their formula one or another of the various commercial fats as shortening agents. It is primarily this added fat which deteriorates and causes the product to spoil. Thus at first glance it would seem logical that the keeping ability of baked products would be related directly to the keeping ability of the shortening used. However, this has not been found to be the case by a number of investigators (Triebold and Bailey [1932-a], Bohn and Olson [1934], and others).

In 1932 Dr. Bailey and myself reported on a study of the keeping ability of 35 commercial cracker samples and the shortenings used in them, secured from as many cracker bakeries scattered over the country. We found that while in general the better keeping crackers were made with shortenings of good keeping qualities, there were several notable exceptions. In certain instances shortenings with poor keeping ability produced crackers with good keeping quality while in other instances the reverse was true.

In an attempt to find an explanation as to why good keeping quality crackers could be produced from a shortening exhibiting poor keeping ability (as indicated by accelerated oxidation studies), lard samples were oxidized to varying degrees of oxygen absorption and used as shortening agents in crackers (Triebold, Webb and Rudy [1933]).

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TABLE 1

Comparison of the Length of Induction Period of Experimental Crackers Containing Open Kettle Rendered Lard Oxidized to Different Degrees with the Length of Induction Period of the Lard, and also, the Peroxide Values of the Lards and the Extracted Fat from the Crackers. Length of Induction Periods Determined by Oxidation in a Closed System at 90°C.

	Lard		Crackers	
	Induction period, hours	Peroxide value*	Induction period, hours	Peroxide value*
Control	3.0	1.6	8.0	1.7
Oxidized to beginning of induction period	0.75	3.6	8.0	5.8
Oxidized to 15 cc. O_2 absorption per 100 grams lard	0.0	14.7	8.0	5.0
Oxidized to 50 cc. O_2 absorption per 100 grams lard	0.0	39.5	8.0	3.2

*Ml. 0.002 N $Na_2S_2O_3$ per gram of fat.

The results of this study are tabulated in Table 1. Apparently the pro-oxygens formed by oxidation of the fat are destroyed in the processing of the crackers, and the keeping ability of the fat is restored to its initial fresh condition. Thus, it appears that the inherent keeping ability of the fresh lard, conditioned by its fatty acid composition and structure, is important information to have on a fat. This has been substantiated by Bohn and Olson (1934), who concluded from their work that "in the shortenings themselves we may have stability affected by both factors, antioxidants and pro-oxidants or fatty acid composition. When we make crackers, however, we find that in general stability depends chiefly on the chemical composition of the fatty acids."

Since our usual accelerated oxidation tests determine the keeping quality of a fat as a function of its content of antioxygens and pro-oxygens, as well as its chemical composition, it is obvious why such tests may be in error when relating the keeping quality of a shortening to a baked product in which the shortening is used. Thus there is need for a good test on shortenings to give the anticipated keeping ability of baked goods using those shortenings.

Flour. Twenty years ago the flour salesman blamed the shortening and the shortening salesmen blamed the wheat oil in the flour when the baker's crackers became rancid. This intrigued me at the time and a simple experiment resulted (Table 2, Triebold [1931]).

TABLE 2

Effect of Wheat Oil Present in Cracker Flour on the Keeping Quality of Crackers

Sample	Length of induction period in hours*
Crackers from untreated flour	7.0
Crackers from ether treated (not extracted) flour	7.0
Crackers from extracted flour	3.0
Prime steam lard shortening	4.5

*Crackers and shortening oxidized in a closed system at 90°C.

A flour was extracted with ether while another sample of the flour was treated with ether but not extracted. These two flours, together with the original untreated flour, were baked into crackers using a lard shortening with an induction period of 4.5 hours (subjected to oxidation in a closed system at 90°C.). The crackers from the untreated flour had an induction period of seven hours when subjected to the same oxidizing conditions as the shortening, showing that there were apparently natural antioxidants present in the flour. The ether treated, but not extracted, flour also produced crackers with an induction period of seven hours, showing that the ether treatment did not affect the flour. The ether extracted flour produced crackers with an induction period of 3.0 hours, which was less than the induction period of the original shortening. The presence of natural antioxidants in the ether soluble fraction of cereal products is, of course, well recognized at the present time, and several patented antioxidants of that general source are on the market.

The possibility of enzymes, particularly oxidase and peroxidase enzymes, accelerating fat oxidation in baked products has been suggested by Carlin and Lannerud (1941). They found that raw potato extract used in a cracker sponge decreased the keeping ability of the resulting crackers. More information on this point would be desirable.

Water. Water has a stabilizing effect on fats (Holm and Greenbank, 1924), on cereals (Fine and Olsen, 1928), and on crackers (Triebold and Bailey, 1932-b). Apparently a certain minimum amount of water is necessary to prevent rapid oxidation of the fat as quantities greater than this amount do not improve the keeping quality. This may mean that the presence of "unbound" or "free" water is necessary to stabilize the product.

Salt. Little information is available relative to the effect of salt on the keeping quality of baked goods. Wilder and Lindow (1937) found that cereal flakes processed without salt were less likely to become rancid than when the normal process involving salt was used. Elder (1941) found that the stability of wheat germ oil was markedly lowered by shaking and cooking with dilute salt brine. Several hypotheses have been advanced to account for this effect, but none have been confirmed. There is need for more information on this subject.

Sugar. Bohn and Olson (1934) state that sugar is a powerful antioxidant. However, the quantity of sugar required to show strong antioxidant properties is so large that it could never be added solely for that purpose. The stability imparted by the sugar is incidental to the use of sugar as a sweetening agent in certain products. This is no doubt one of the reasons why rancidity in cookies is not as prevalent as in crackers.

McKinney and Bailey (1941) also found sugar to have a strong antioxidant effect when added to a biscuit formula in the amount of one-fifth of the weight of the flour used in the formula. They found sugar to exert a protective factor of 5-6 when oleo oil, hydrogenated lard, or hydrogenated vegetable oil was used as a shortening agent in the formula. Sugar only exerted a mild antioxygenic effect (protective factor of 1.5-1.6) when used with prime steam lard in the formula.

Antioxidants. The addition of antioxidants to fats has been found in a number of cases to improve tremendously the keeping qualities of the fats. However, the carry-over of this effect into baked products has not been too satisfactory.

Bohn and Olson (1934) experimented with two antioxidants used for stabilizing lard and found that while both were effective in the lard itself, the one was completely lost when the lard was used in crackers. The other was somewhat effective in the crackers produced, which however still lacked the keeping qualities of crackers produced with good hydrogenated shortenings.

Oat flour and oat flour extracts were found to have but a slight favorable effect on the keeping qualities of crackers (Triebold, 1938). The oat flour and extracts were added to the cracker sponge, in doughing up the sponge, or sprayed or dusted upon the baked crackers. A protective factor from 0 to 2, which for all practical purposes is negligible, was exerted by the various treatments.

Lundberg, Halvorson, and Burr (1944) found that NDGA (nordihydroguaiaretic acid) when added to a lard used in making pie crusts and soda crackers exerted some stabilizing effect on the resulting product (protective factor of approximately 2 in crackers and 10 in pie crusts). The lesser effectiveness of the NDGA in crackers was thought to be due to the alkalinity imparted by the baking soda since alkaline solutions of NDGA oxidize rapidly when exposed to air.

Higgins and Black (1944) studied the effect of several antioxidants added to lard used in the preparation of crackers. They found gum guaiac to be an effective antioxidant for lard with the stability carrying over into the baked product (protective factors of 2.5-7, depending upon concentration). Propylgallate exerted a stabilizing effect on the lard but practically none on the resulting crackers. The same was also true for the tocopherols and for a wheat germ oil derivative (an ethylene dichloride extract of wheat germ oil combined with citric acid).

Mixing, Fermentation and Baking. These manipulative procedures involved in the manufacture of baked goods likely play a role in the keeping quality of the resulting product. This has been referred to previously in the destruction of pro-oxidants and antioxidants present in a fat when baked into crackers. Mixing spreads the fat over a greater area and also in the presence of salt may cause the solution of certain fat components into the aqueous phase, thereby facilitating their oxidation later. Fermentation produces sugars and organic acids, and these may have an effect upon the stability of the shortening.

The temperature and length of baking time might be anticipated to have an effect on the stability of the fat in baked products. Apparently as long as there is sufficient moisture present so that the product does not scorch, the effect is not great. However, crackers with scorched spots or crackers that have been crisped by successive reheatings show a marked decrease in keeping quality.

Packaging. The possibility of the absorption of fat from a baked product by the package must not be overlooked. The lining of cracker packages with grease-proof paper has helped greatly. However, some baked products are packaged in cardboard boxes. In such packages the fat may be absorbed rapidly by the cardboard, thereby spread over a large surface, and consequently undergoes rapid oxidation. This emphasizes the need for proper packaging to insure a good keeping quality product.

Several patents have been taken out on the impregnation of cardboard packages and wrappers with antioxidants and these are used to some extent. In certain instances these have proved helpful in retarding spoilage of the products contained, while in other instances they have been ineffective.

The use of colored glass to cut out the blue and ultraviolet rays of light was suggested by Burr (1907) as a means of protecting dairy products from oxidative deterioration. This has led to the development and effective use of colored cellophanes for packaging food products that will be exposed to light when merchandized.

Summary. In summarizing, it would appear that effects on the stability of cereal products to oxidative deterioration by formula components as well as methods of processing, are not understood to the degree that they should be and that there is a great need for studies along these lines.

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Toxicity of Rancid Fats*

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THE scientific literature contains a number of reports of malnutrition resulting from rancid dietary fat. The symptoms include ophthalmia, gastric papillomatosis, and other digestive disturbances, reproductive failure, anemia, dermatitis, and cancer. In some cases the symptoms have been attributable to known deficiencies. Some others are not so readily explained even in terms of present knowledge. Whether rancid fats exert a direct toxic action is also uncertain.

First, I should like to discuss briefly some effects which oxidized fats are known to produce through the oxidation of dietary essentials, especially the vitamins. The five fat-soluble dietary essentials, linoleic acid, tocopherol, vitamins A, D and K, are susceptible, though not equally so, to oxidation. Tocopherol and vitamin A are the least resistant, and their oxidation is accelerated by the peroxides of linoleic acid. It has long been recognized that dry foods or food materials containing them lose their potency on continued exposure to air. Recently it has been shown (1, 2) that even when these materials are fed in fresh condition, they may lose potency in the digestive tract

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