

Causes of Deterioration of Fats and Oils

*Exceedingly Small Changes Caused by Oxidation and by
Micro-organisms are Sufficient to Produce Detectable Taints*

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IN THE case of edible fats and oils it can be generally stated that tests by taste and smell afford evidence of deterioration before it can be supplied by any delicate chemical test. There is, therefore, much room for investigation of conditions in a fat or oil which lead to its rapid deterioration. Our present knowledge is such that we can only detect rancidity and other taints, once they have commenced in the fat, by delicate tests for small amounts of end-products. There is no test available whereby two fats, say, could be tested for length of time within which they are likely to remain in a wholesome condition and there is no reliable test whereby one fat might be proved to have a lower keeping quality than another. What is required is a reliable method of detecting the *tendency* to deterioration before such deterioration is evidenced by taste and smell (*i.e.*, by organoleptic tests).

It is obvious that chemical tests for deteriorated fats are only of secondary or confirmatory importance if the deterioration has already been detected by the senses. As will be explained later, once deterioration of a fat has commenced the rate of its development is increased owing to the reaction being autocatalytic. Economically, the ideal test would be one on the fresh material, for the purpose of determining the comparative possibilities of future deterioration. Material showing poor keeping properties could either be consumed quickly or utilized for a purpose where future deterioration would either be checked or masked, whereas the material of good keeping quality could be kept for a favorable market or conveyed to localities of a character requiring such material. In any case, the risks attendant on deterioration of a material could be minimized were such a test for fresh material possible.

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Nature of Deterioration

FATS and oils may be said to suffer deterioration from two main causes:—(a) Oxidation by atmospheric oxygen; and (b) Biological causes, through the agency of micro-organisms.

Oxidative deterioration sets in through the action of atmospheric oxygen, influenced by heat, light, acidity and the effect of catalysts, on the fat. Certain products are formed in the initial stages which spoil the taste and smell of the fat: the fat is termed "slightly off," after which deterioration proceeds rapidly to give a badly colored tallowy product.

Biological deterioration is the result of the activities of micro-organisms which contaminate the fat or oil. Although fat is not the ideal medium for general micro-organic growth, when contaminated it can support a modified form of growth where the metabolism of the micro-organisms is greatly changed from the normal. Certain products, *e.g.*, ketones and lower acids, are formed which confer an off-flavor, and such fats are termed rancid, or acid. By far the worst effect is that of various moulds which can form methyl ketones from the lower fatty acids; *e.g.*, from coconut oil by the action of the dry moulds (*Penicillium*, *Aspergillus*, etc.) there are produced methyl-amyl up to methyl-nonyl ketones, the odors of which confer on rancid coconut oil its repulsive smell.

Oxidation of Fats

THERE is conclusive evidence that the "chemical" deterioration of fats is due to oxidation, and that the primary effect is associated with the double bonds of the unsaturated fatty acid radicals of the esters composing the fat. This has mostly been studied with reference to the oxygen uptake of fats at constant temperature. When a sample of fat in contact with air or oxygen is connected to a

manometer and the absorption of oxygen with time measured, it has invariably been noticed that an appreciable period of time elapses before any measurable quantity of oxygen is taken up. This period, called the "period of induction," is the period required by the system to undergo activation and reach that "potential" necessary for the subsequent oxidation to occur. When this period is a prolonged one, as is found to be the case for pure, acid-free fats, a very small amount of oxygen is taken up, the tendency of the system to remain in the unoxidized state of the double bonds (of oleic and other unsaturated acids) being gradually overcome. Once the period of induction has been overcome, oxygen absorption increases at a measurable rate. The rate of absorption subsequently increases logarithmically, which indicates that the products of oxidation catalyze subsequent oxygen absorption; that is, the oxidation is auto-catalyzed. Even with ordinary fats at room temperature, the period of induction is very long, but by working at higher temperatures, *e.g.*, at 60° to 95° C., the period can be shortened to a few hours, depending on the state of the fat. In the subsequent logarithmic absorption, every 10° C. rise of temperature doubles or trebles the rate of absorption.

The practical significance of this period of induction is that it normally represents the time during which a fat will keep in a wholesome condition, and provided the fat is consumed or otherwise utilized within this period (prolonged, of course, at ordinary temperatures for pure fats and oils) deterioration will not occur. But conditions in the fat and in the storage of the fat have an effect in shortening this period.

Conditions Affecting Oxidation

THE conditions likely to catalyze the subsequent oxidation of fats have also the effect of shortening the induction period. These conditions enable the fat to reach the "trigger" stage in quicker time. Briefly the conditions favorable to a shorter induction period are:—Heat, light, acidity, other impurities and metallic catalysts; and the effect of very small traces of metals such as iron and copper has been found to be far greater than the effects of all the physical factors put together.

A higher temperature of storage has been found to shorten the period of "wholesomeness" of a fat. The increased mobility of the molecules, and a higher energy content of the system at the higher temperature, are undoubtedly the factors operating. The benefits of cold storage are evident.

Storage in glass vessels in sunlight causes a fat to oxidize much more quickly than if it is stored in opaque containers in the dark. Subsequent oxidation is also photo-catalyzed. Ultra-violet radiation is the cause of this difference. (The finely-dispersed fat in milk can deteriorate sufficiently on an exposure of two minutes to the radiations of a small mercury vapor lamp as to be detectable by taste; while after a ten minutes' exposure the milk is almost undrinkable.)

The higher the free-fatty-acid content of a fat, the shorter will be the induction period. The slow hydrolysis of fat which proceeds in the presence of free fatty acid, thus liberating other acids and glycerol, may be regarded as the cause of this phenomenon, particularly when the free acid is, as usual, predominantly oleic; and the simplification of the oxidizable molecule and its dispersion by mutual solution through the fatty phase are factors in hastening the period of induction. The effect in catalyzing the proper oxidation later is more marked than the others where acidity is concerned.

Effect of Other Impurities

L IPOIDS, usually found in association with fats proper in fats of biological origin before refinement, are conducive to a shortened period of induction. The lipoids are more active chemically than the fats, and are likely to suffer oxidation first. They are also more soluble in neutral salt solutions and other aqueous phases found in small quantities in all unrefined fats. The unsaturated fatty acids in the lipoids are therefore oxidized sufficiently to bring about a shortened period of induction. Where there is sufficient lipoid present in the fat to make its products of oxidation noticeable by taste or smell, an intermediate "taint" occurs. The lecithin of butter is quickly oxidized, the chlorine residue evolving noticeable traces of trimethylamine, resulting in the "fishy" flavor of cold-stored butter in commerce. The "fishiness" of butter is subsequently followed by "tallowiness," or oxidation of the fat proper, and bleaching of the pigment.

The occurrence of "foots" or "marc" in unrefined oils tends, for a variety of reasons, to make the period of induction shorter. The "foots" usually contain a lipase (which increases the acid value of the fat), and also free acids, which tend to liberate fat-soluble fatty acids, *e.g.*, oleic acid. The "foots" also contain protein decomposition products, which enter the trace of aqueous phase of the future refined material. The "foots" also are seats of normal micro-organic growth. The same ef-

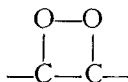
fect of non-fatty organic material in animal fats may be cited. Although, in cold storage, micro-organic growth may be depressed to a minimum, yet the products of micro-organic activity in contact with the fat accelerate the chemical action even at the low temperature.

By far the most potent agents inducing fat deterioration are small traces of metallic catalysts, present as soaps or other salts in the fat, which have entered the fat during processing or refining. The amount of metal necessary to bring about this deterioration is of the order of 0.5 to 10 parts of metal per million parts of fat, so that it can be seen that care in the use of metallic plant exposing copper and iron surfaces is essential. Copper is the most potent metal in this respect, while iron, manganese, nickel and cobalt are injurious, though less so than copper. For example, butter stored at 15°C. and containing 5 parts per million of copper (as lactate) developed tallowiness in 7 days, whereas 50 parts of iron per million was necessary to make the same butter tallowy in 9 days. The sample containing iron gave the intermediate taint of fishiness in 2-4 days. A control sample remained sound for six weeks (until moulds had shown their effects).

Acidity of the fat during refinement leads to a greater solution of injurious metals from containers and plant during processing, so that the refining of oils and fats at as low an "acid value" as practicable is advisable. The injurious metals undoubtedly act as oxygen-carriers, and, during the period of induction, very quickly confer on the system that "potential" necessary for the oxidation proper to occur. Their activity, once oxidation has started, is evident from the subsequent rapid deterioration of the fat.

Cause of Deterioration

THERE are many versions of the theory put forward to explain the auto-catalytic oxidation of fats. The primary step consists of the addition of a molecule of oxygen to the double bond of an unsaturated acid, *e.g.*



Thus, oleic acid forms oleic acid peroxide. This peroxide might break up in a variety of ways:—(a) A small amount of water might react with it, forming hydrogen peroxide, which would oxidize any foreign material, *e.g.*, protein degradation compounds or inorganic lipid residue as in lecithin, or attack glycerine or a further fatty acid radical in the fat; (b) Water would react forming dihydroxystearic acid and

liberating one atom of oxygen which could be used for further oxidation or the formation of an ozonide of an oleic acid molecule remote from a water film; (c) The oleic chain might be broken at the oxidized double bond to give nonaldehyde and azelaic semialdehyde—further oxidation of which would give nonoic and azelaic acids respectively; (d) β -oxidation of the portions of the broken oleic acid chain could give acids with two carbon atoms per chain less, *e.g.*, heptylic aldehyde or acid from nonaldehyde or nonoic acid; (e) The saturated fatty acids could be broken down in a similar manner to that of nonoic acid, to give a series of acids each differing by two carbon atoms.

Although reactions such as the above would result in the breakdown of some of the fat molecules, and should be detectable by a change in the constants of the fats (*e.g.*, iodine value), it must be borne in mind that the amount of change necessary to give a taint noticeable by taste and smell need only be very small, and such changes usually cannot be detected by changes in the fat constants. Indeed, very advanced deterioration is necessary before any appreciable and significant change in acid value, iodine value, or hydroxy-acid content can be observed in the fat under investigation.

In the case of linoleic and linolenic acids, whenever these are present in fats in small quantity, the short-chain compounds formed by the ruptures of the chains at the double bonds give compounds which enable the chemical tests for confirming oxidative deterioration to be carried out sooner than with fats free from these acids. The Kreis test, which will be described later, is thus useful for fats containing these acids. (Where large amounts of these acids are present, the fats exhibit the characteristics of drying oils, in being capable of forming a high content of hydroxy acids. These confer a quasi-carbohydrate nature on the molecules, enabling the mass to polymerize to a hard resin-like substance.)

(To be continued)

Wetting, cleansing and dispersing agents are composed of condensation products of fatty acids of high molecular weight and aliphatic, aromatic, hydroaromatic or heterocyclic amines or their derivatives or substitution products, along with soap or soapy substances such as Turkey red oil or sulfonic acids. Fr. Pat. No. 682,227.