Peroxide Formation as a Measure Of Autoxidative Deterioration

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In spite of the enormous amount of valuable research which has been reported on the subject, the nature of the chemical reactions involved in the deterioration of vegetable oils is yet largely conjectural. Many phases of these reactions have been examined; the products produced during deterioration; analytical methods of determining these products; the factors influencing the reaction rates, and other aspects of the whole phenomena of rancidity have been carefully considered. A complete review of all this work would be beyond the scope of this paper. However, an attempt is here made to bring together that material from the literature of rancidity which bears upon the investigation reported below.

Oxidation by the oxygen of the air, aided by such agents as light, heat and certain metallic or organic compounds, is generally considered responsible for the development of rancidity. (Such a case, where molecular oxygen enters into a chemical reaction is termed “autoxidation.”) While bacterial action has been considered as a possible factor it is now generally conceded that the primary change occurring during the aging of an oil or fat is a strictly chemical oxidation. The majority of investigators have therefore directed their attention towards means of studying both quantitatively

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and qualitatively the action of oxygen and the products formed during the deterioration.

Greenbank and Holm\(^4\) studied the susceptibility of fats towards autoxidation by measuring the rate of oxygen absorption by a given amount of fat or oil under reproducible conditions. This technique has been used in modified forms by other workers for studying autoxidation.\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\)

A recent improved apparatus for following oxygen absorption is described by Milas\(^11\) in which he overcomes the following objections to previous methods:

1. Changes in rate of absorption due to changes in pressure of the oxygen.
2. Failure to maintain a true equilibrium between the oil and oxygen gas.
3. Formation of oxidation products which may be gases and hence decrease the apparent absorption rate. The presence of volatile products which may otherwise affect the reaction.

The apparatus used to correct these errors is, of course, quite complicated.

Another method of following the amount of oxygen absorbed is by observing the gain in weight of an oil on exposure to oxygen. Delore\(^12\) used this procedure to compare several oils. Traufer and Müller\(^13\) also employed it as a means of comparing certain known methods now used for qualitatively measuring rancidity. The use of the gain in weight method as a true index of the amount of oxygen absorbed during the development of rancidity is also open to objections. Browne\(^14\) has demonstrated in the case of butter fat that volatile products may escape, causing a loss in weight; further, that hygroscopic substances may be formed which take up moisture from the air, thus causing an increase in the weight result obtained.

A third method of attack upon the problem of autoxidation has been made by taking advantage of the fact that some of the reducing substances produced (presumably aldehydes) are volatile and may be removed from the oils or fats by steam or air currents. The quantity of these products may then be estimated, at least comparatively, by determining the amount of permanganate necessary to oxidize them. Issoglio\(^15\)\(^16\) appears to be the first to have used this procedure. More recently Grettie and Newton\(^17\) have described an improved apparatus for such a determination.

A general variation on the above method consists in detecting the aldehydes without removing them from the oils or fats. The von Fellenberg\(^18\) test for aldehydes using the familiar fuchsinsulfur dioxide reagent under definite concentrations and conditions is such an example. The test has been given a quantitative aspect by comparing the color depth produced to that produced by known concentrations of acetaldehyde under similar conditions. The values are, of course, reported in terms of acetaldehyde units. Arbitrary color standards have also been used made from permanganate solutions. It has been objected (cf. ref. 13) that this test is too uncertain for a quantitative method, and in general it does not seem to have attained great popularity. This may be due to