contents of the dish. Evaporate to dryness on the steam bath. Ignite the contents of the dish over a bunsen flame until the organic matter is destroyed. Allow to cool.

Transfer the dish to a 600-ml. beaker and add 200 ml. of water. Warm on a hot plate to facilitate solution of the fused mass. When solution is complete remove the dish with forceps and wash with water adding the washings to the solution already in the beaker.

Add 5 ml. of 50% NaOH solution and proceed to precipitate with $SrCl_2 \cdot 6H_2O$ as previously directed. Titrate with N/20 NaOH in the presence of mannitol.

Table VI shows some of the results obtained by this procedure. All samples contained approximately 10% of Na_2SiO_3, Na_2SO_4, and $Na_4P_2O_7 \cdot 10H_2O$; approximately 55% of the detergent and the indicated amounts of hydrated borax.

TABLE VI.

Recovery of Borax Added to Synthetic Detergents.

Type of Synthetic Detergent*	$Na_2B_4O_7 \cdot 10H_2O$ Added	$Na_2B_4O_7 \cdot 10H_2O$ Recovered
	%	%
Aliphatic Sulfate—Sample I	13.00	12.78
Aliphatic Sulfate—Sample II	10.00	10.10
Aliphatic Sulfate—Sample II	10.15	10.24
Aliphatic Sulfate—Sample II	10.34	10.37
Fatty Acid Amide	8.50	8.52
Alkyl Aryl Sulfonate	11.55	11.70
Non-Ionic Compound	9.24	9.44
Cation-Active Compound	6.53	6.60

*All samples contained approximately 55% of the synthetic detergent; approximately 10% of Na_2SiO_3, Na_2SO_4 and $Na_4P_2O_7 \cdot 10H_2O$ and the indicated amounts of hydrated borax.

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Flavor Reversion in Edible Fats[1]

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FLAVOR reversion in fats is probably defined most satisfactorily as the appearance of objectionable flavor from less oxidation than is required to produce true rancidity. The degree to which reversion and rancidity are separated—in terms of oxygen absorbed by the fat—is widely different for different fats. In the broadest sense, no fat is altogether free of a tendency toward reversion, i.e., there is none which will remain completely neutral in flavor up to the point of incipient rancidity. Most fats, however, do not develop markedly objectionable flavors or odors until oxidation has become relatively far advanced. In these the onset of reversion and of rancidity are so nearly coincidental that reversion constitutes no special problem. There are some fats, however, including particularly fish oils and vegetable oils containing linolenic acid, which revert with extremely slight oxidation. It is almost impossible to prepare edible products from such fats and get them to the consumer before they have suffered some loss of palatability. It is the reversion occurring in these fats which is of greatest present interest and will be principally treated in this discussion.

[1] Presented at the Conference on Problems Related to Fat Deterioration in Foods under the auspices of the Committee on Food Research. Research and Development Branch, Military Planning Division, Office of The Quartermaster General.

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It has been pointed out previously (1, 4, 11) and should be repeated that the term "flavor reversion" is to a large degree a misnomer. Probably the term originated in reference to marine oils, which have a fish-like flavor and odor until they are deodorized and upon reversion again assume a decidedly fishy character. Most other fats which are given to reversion, particularly hydrogenated fats, have flavors and odors in the reverted state which bear little or no resemblance to the flavor or odor of the unprocessed fat. Thus, unhydrogenated soybean oil which has reverted badly is more "fishy" than "beany." Hydrogenated soybean oil in the reverted state has a flavor which is reminiscent of hay or straw. The reverted taste of hydrogenated linseed oil is more or less similar to that of hydrogenated soybean oil, but more pronounced. Hydrogenated rapeseed oil develops a peculiar nauseous taste, suggestive of an animal odor.

Amount of Oxygen Required to Produce Flavor Reversion

The extremely small amount of oxidation which may be required to produce reversion is well illustrated by certain experiments carried out on hydrogenated lard (2). Slightly hydrogenated lard (i.e., lard hydrogenated from an iodine value of about 70 to about 60) has the peculiarity of quickly developing a muttony flavor only when stored in a sealed can

or other container with a limited supply of oxygen. In these experiments a freshly deodorized fat was stripped with oxygen-free nitrogen under reduced pressure, to remove all dissolved gases, and portions were then sealed in tin cans with nitrogen containing variable and known amounts of oxygen in the headspace. When oxygen was wholly excluded from the cans, there was no flavor deterioration in samples stored at 98° F. for as long as 18 months. However, in the presence of as little as 0.5% oxygen on the basis of the volume of the fat, reversion to a muttony flavor occurred within a few days. The absorption of about 25% of oxygen was required to produce rancidity in this fat. It can be calculated, therefore, that even if the test sample absorbed all of the oxygen in the headspace, the oxygen sufficient to produce reversion amounted to no more than one-fiftieth of that required to produce rancidity. Actually, the amount absorbed was probably very much less.

Subsequent work demonstrated that commercial nitrogen, which contains 0.5% or more of oxygen, is not pure enough to be used in the headspace of sealed cans containing this product. The solubility of air in fats is sufficiently high (*ca.* 8% by volume at room temperature) that hydrogenated lard exposed to the atmosphere will dissolve many times the amount of air required to bring on reversion.

The degree of oxidation required to produce flavor reversion in raw or hydrogenated linolenic acid oils appears to be of a similar order of magnitude. It is often observed that hydrogenated soybean oil with a very satisfactory stability toward rancidity—an oil, for example, with a Swift keeping time of 100 to 200 hours—will become reverted through standing for a few days, or even hours, at room temperature. Robinson and Black (11) reported that reversion occurred in hydrogenated soybean oil when the fat was stored under an inert gas with almost complete exclusion of oxygen. Bickford (4) observed that flavor deterioration took place under certain conditions in unhydrogenated soybean oil which had been degassed and sealed in tubes under the vacuum created by a mercury vapor pump. He suggested that in this case oxygen might be provided through an intramolecular mechanism in the oil.

The respective phenomena of flavor reversion and rancidification are associated with amounts of oxidation so different in degree that it appears hardly proper to consider the two as more than casually related. There is little in our present knowledge of rancidification and its prevention that seems to bear very usefully upon the reversion problem. In inhibiting reversion the expedients usually adopted to enhance stability—the use of antioxidants, reduction of unsaturation by means of hydrogenation, or packaging to minimize access of oxygen—are in general of small avail.

Flavor Reversion in Unhydrogenated Oils

As will be explained later, there is reason to believe that flavor reversion in unhydrogenated oils may result from a mechanism different from that operating in the same oils after hydrogenation. The two classes of oils will, therefore, be considered separately.

The common oils in which reversion occurs to a pronounced degree include all of the marine oils, soybean oil, linseed oil, and rapeseed oil. Among the oils of roughly equivalent unsaturation which do not revert are corn oil and sunflowerseed oil. When the reverting oils as a class are compared with the non-reverting oils, with respect to chemical composition and other possibly pertinent factors, one fact is strikingly evident. All of the reverting oils contain linolenic acid or other unsaturated fatty acids with more than two double bonds. None of the non-reverting oils have any considerable content of fatty acids more unsaturated than linoleic. It seems very likely, therefore, that reversion is at least partially inherent in the glycerides of the oils and is associated with the presence of fatty acids containing more than two double bonds.

It would appear, however, that highly unsaturated fatty acids are not solely responsible for all cases of reversion, but that in some instances, at least, non-glyceride constituents of the oil are involved. This is particularly true of fishy flavor and odor, which can scarcely arise except from compounds containing nitrogen. Fishiness occurs not only in marine oils but is also the almost invariable result of advanced reversion in soybean and other linolenic acid oils. It may also occur in butterfat.

Davies and Gill (5) have shown that fishiness in oils is associated with nitrogenous compounds entering into chemical combination with the oil during the course of autoxidation. In one experiment involving treatment of samples of oil with trimethylamine oxide, fishiness was produced in linseed oil but not in olive oil. This would indicate that under certain conditions the development of fishiness requires the presence of highly unsaturated fatty acids. In a series of fish oils derived from decomposing material intensification of the fishy flavor and odor was paralleled by an increase in the amount of nitrogen bound by the oil. Binding of nitrogen by the oil was also accompanied by the development of dark colors.

Since traces of phosphorus remain in soybean and other vegetable oils even after caustic refining, it may be that phosphatides are the source of nitrogen and hence of fishy flavor. Lard, which does not ordinarily develop fishiness, is often observed to do so after the addition to it of commercial lecithin as an antioxidant. There is evidence, however, of other nitrogenous compounds in seed oils. Thus, Thornton and Kraybill (13) found that adsorption refining of crude soybean oils resulted in almost complete removal of phosphorus from the oils but left approximately one-third of the nitrogen. They suggested that the residual nitrogen might be in the form of compounds resulting from the decomposition of phosphatides during processing of the beans.

The observations reported by Sanders (12) suggest that the flavor instability of soybean oil in general may correspond to the degree to which deteriorative processes have been allowed to take place in the beans prior to expression of the oil. A large number of oil samples, both before and after hydrogenation, were found consistently to decrease in flavor stability with increase in the color of the oils after refining and bleaching. Carotenoid pigments, which are probably responsible for most of the color of vegetable oils of good quality, are removed from oils by adsorption with relative ease. It may be presumed, therefore, that the color remaining in soybean oils after refining and bleaching treatment is to a large extent derived from decomposition products of the seed. Obviously, such products do not appear only

during processing of the beans but may accumulate in the beans prior to processing. So-called field-damaged beans have very high contents of difficultly removable pigments, and, according to Sanders, yield oil of very inferior flavor characteristics.

Flavor Reversion in Hydrogenated Oils

The present discussion of flavor reversion in hydrogenated oils will be limited to soybean and linseed oils. Presumably, reversion in hydrogenated marine oils is comparable to reversion in the vegetable oils which contain highly unsaturated acids.

At present the particular case of reversion which is of much the greatest practical concern is that occurring in hydrogenated soybean oil. The reverted flavor and odor of this oil is hay-like or straw-like. Even when not strong, it has a peculiarly persistent quality and leaves an after-taste in the mouth. When not overly pronounced in a food, the reverted flavor may pass unnoticed while the food is being eaten; but later it may become unpleasantly apparent. It is accentuated when the fat is heated during frying or baking. A test for reverted flavor much used in the industry comprises heating the fat to a smoking temperature, scrambling an egg in it, and tasting the egg. Different individuals differ markedly in their sensitiveness to this flavor and in the degree to which it seems distasteful to them. Experience in the distribution of soybean oil-containing shortenings throughout the United States has revealed that it is much better tolerated by consumers in some sections than in others.

In all-hydrogenated shortenings or margarines in which soybean oil is mixed with cottonseed oil or similar non-reverting oils, detectible reversion does not occur in the mixture unless the soybean oil exceeds a certain critical proportion of the whole. This proportion varies somewhat according to the initial quality of the oil and probably also the methods used in processing it but is generally between about 25 and 35%. The reverted flavor of hydrogenated linseed oil is much stronger than that of soybean oil, as might be expected from the greater linolenic acid content of linseed oil. In both soybean and linseed oils the tendency to reversion is largely or entirely eliminated by continued hydrogenation of the oil to an iodine value of about 45 to 50. At this point, however, the oil becomes much too hard and high-melting for edible use, unless it is blended with a softer oil.

Since flavor reversion in unhydrogenated oils appears to be definitely associated with the presence of highly unsaturated acids and since the property of reverting is destroyed only by prolonged hydrogenation, it was once suspected that the hydrogenation of linolenic acid might not proceed selectively and that small residual proportions of this acid might be responsible for the reversion occurring in partially hydrogenated oils. At the time that flavor reversion in hydrogenated soybean oil first became a problem there was no reliable method for detecting traces of linolenic or other highly unsaturated acids in oils, and hence of checking this hypothesis. Lately, however, the spectral method developed by Mitchell, Kraybill, and Zscheile (9) and by others has provided a delicate and certain means for estimating these acids. It has been found that linolenic acid does not in fact hydrogenate quite as readily as might be expected from its high degree of unsaturation (3). Nevertheless, in soybean oil it absorbs hydrogen about twice as readily as linoleic acid, and in oil selectively hardened to the consistency of shortening or margarine it is not present in detectible amounts.

The circumstances outlined above combine to point to the probable existence of an unsaturated compound responsible for reversion which is not linolenic acid, but of which linolenic acid is a precursor. The recent and possibly very significant series of experiments carried out in Canada by Armstrong and McFarlane (1), and more particularly those carried out by Lemon (8) have produced the first definite evidence regarding the identity of this hypothetical compound. The analysis of samples of hydrogenated linseed oil with the assistance of the spectral method revealed the presence of considerable proportions of an isomeric linoleic or diethenoid acid which did not yield a conjugated system of double bonds upon treatment with alkali, and which, therefore, could be presumed to be a 9:10, 15:16 acid, produced by the hydrogenation of linolenic acid at the middle or 12:13 double bond. The disappearance of flavor reversion in the hydrogenated oil coincided with the disappearance of this so-called isolinoleic acid. Furthermore, distilled concentrates of the isolinoleic acid as well as pure methyl linoleate subjected to hydrogenation developed the typical reverted flavor and odor when heated.

It would appear, therefore, that reverted flavor in hydrogenated oils, possibly unlike that occurring in unhydrogenated oils, may be simply a product of the glycerides of the oil and not of the glycerides combined with nitrogenous compounds or other non-glyceride constituents. However, the observation of Sanders (12) that even in hardened oils high bleach colors correspond to poor flavor stability cannot be ignored. Certainly, if non-glyceride materials are invariably involved in the flavor reversion of hydrogenated oil, these materials are not in the unsaponifiable fraction but remain associated with the fatty acids through distillation of the free acids or molecular distillation of the glycerides. Possibly the presence of such substances serves merely to accentuate the reverted flavor.

It is unfortunate that there is at present no reliable means of detecting or estimating traces of nitrogen in organic materials such as fats and oils as a correlation of flavor stability data with nitrogen analyses would be of much interest.

Present knowledge of the reversion phenomenon is too limited to permit any hypothesis to be advanced regarding the mechanism of reaction between oxygen and isolinoleic acid or other materials to produce the compounds actually responsible for flavor and odor. The concentration of the latter in the reverted oils is so extremely low that it will undoubtedly be very difficult to bring about their isolation in amounts sufficient to permit identification.

As pointed out by Lemon (8), there is some reason to hope that a solution to the problem of reversion may eventually be found in an improved hydrogenation process. Several recently issued patents claim special techniques which produce hydrogenated soybean oil with superior flavor stability. The method of Durkee (6) involves hydrogenation of the oil at a low pressure, with a low concentration of catalyst and with low agitation, until its iodine value has been reduced two to four units. After this limited treat-

ment with hydrogen, the oil is said to be still suitable for use as a salad oil. The essential feature of the method patented by Gudheim (7) is the use of a very low hydrogenation temperature, i.e. a temperature below about 110°C. Paterson (10) subjects the oil first to treatment under conventional hydrogenation conditions and thereafter hydrogenates with a catalyst of the copper chromite type, under high pressure. The principal object in his process is a high degree of decolorization of the oil, but improved flavor stability is also claimed.

The suggested role of isolinoleic acid in flavor reversion naturally focuses attention on the possibility of hydrogenating in such a manner as to avoid the presence of this isomer. It is well known that the amount of "iso-oleic" acids appearing in a hydrogenated oil is greatly influenced by the conditions of hydrogenation. The available data (3, 8) do not indicate that it will be possible to eliminate isolinoleic acid in a plastic product hydrogenated under conventional conditions with a nickel catalyst. However, it appears possible to choose conditions that will maintain this acid at a minimum.

Apparently, linolenic acid adds hydrogen with approximately equal readiness at the 12:13 and 15:16 double bonds, regardless of hydrogenation conditions (3). The formation of isolinoleic acid, therefore, seems unavoidable. Once formed, this acid is much more difficult to eliminate by hydrogenation than is normal linoleic acid, apparently because double bonds in the 9:10 and 15:16 positions are too widely separated to exert a mutual activating influence. The degree to which elimination of diethenoid acids is feasible is determined to a large extent by the relative affinities for hydrogen of these acids and the monoethenoid acids (oleic acid) occurring together in the form of glycerides in the raw oil. Whereas under selective conditions normal linoleic acid hydrogenates 20 to 30 times as readily as oleic acid, the 9:10, 15:16 isomer hydrogenates only about three times as readily (3).

Because of the isolated positions of its double bonds, isolinoleic acid behaves similarly to oleic acid and differently from normal linoleic and linolenic acids with respect to selectivity in hydrogenation (3). In the earlier stages of hydrogenation, therefore, isolinoleic acid may be kept relatively low by application of the same conditions that lead to the minimum production of total oleic acids in cottonseed or other oleic-linoleic acid oils (low temperature, high pressure, high agitation, low concentration of catalyst). However, in the latter stages, such conditions may well produce a higher isolinoleic acid content than "selective" hydrogenation conditions, since linolenic acid, the precursor of isolinoleic acid is more quickly eliminated under selective conditions.

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A Direct Volumetric Method for the Analysis of Soap*

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THERE has been no accurate method of directly titrating soap with acid. One obstacle to such titration in aqueous solution is the liberation of fatty acids and acid soaps in a finely divided state, preventing accurate observation of the color change of the indicator. In alcohol the soaps are often not sufficiently soluble and the indicators which must be used do not give a sharp end-point.

It is now found (1) that a mixture of a glycol with a higher alcohol or with a chlorinated hydrocarbon forms a very powerful solvent for any soap, and the solution thus formed admits of a direct titration of the soap by a strong acid dissolved in the same mixed solvent, the end-point being determined by an indicator with a sharp color change. The method is general, being applicable not only to soaps but to practically all weak monobasic acids, as will be discussed elsewhere.

*Presented at the 19th Annual Fall Meeting of the American Oil Chemists' Society, Nov. 7-9, 1945, in Chicago.

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Method and Results

The solvent medium chosen is a mixture containing an equal volume of ethylene or propylene glycol and isopropyl alcohol, the latter being chosen for its easy availability, lower volatility, freedom from toxicity and low viscosity, but any other higher straight-chain alcohol or any chlorinated hydrocarbon may equally well serve the purpose. One gram of the soap is dissolved in 10 to 20 ml. of the solvent mixture. The dissolving is best carried out by first adding the glycol and allowing a few minutes if necessary, by standing in a warm place, for the swelling of the soap. The alcohol is then added and on shaking, the soap dissolves to a clear solution. If the soap contains a large proportion of stearate, chloroform may be used with great advantage in place of isopropyl alcohol as