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PROTECTION OF MINCED OILY FISH AGAINST RANCIDITY

by

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SUMMARY

Considerable advance has been made during the past twenty years in the understanding of the chemical process of oxidation and rancidity, and of antioxidant activity. These developments are discussed, but it is concluded that considerable further fundamental research remains to be done, particularly in connection with specific reactions occurring in different foods, and especially so in connection with minces made from different oily industrial fishes, for which very few tests and hardly any research is reported.

No known antioxidant treatment can compare favourably with the protection against oxidation and rancidity that is afforded by hermetic sealing to exclude contact with oxygen. For very long period storage of raw mince or cooked and pressed mince from fatty fish, whether it is preserved by salting or in the frozen state, the only reliable protection against rancidity is afforded by canning or sealed plastic packaging - not necessarily vacuum sealing. For instance, 50 kilo heat sealed bags made of 0.22 mm thickness sheeting or, for the tropics, hermetically sealed drums would prove suitable. Small retail sized plastic packages can be stored and transported in the larger containers until they are marketed for use within a few months.

Promising long term results have been achieved with antioxidants for other products. While using hermetic packaging for the fish minces in the initial stages, it would seem possible to obtain satisfactory storage with such minced fish using known synergistic mixtures. Oat flour, and/or herbs, and/or spices, and/or lemon oil should be used in fish minces wherever consistent with the end use of the product.

For short term storage for a few months, e.g. after opening (large) hermetically sealed packages, the prospects of successful protection against oxidation seem more encouraging, especially with cooked and pressed mince. Antioxidant mixtures that look the most promising include EQ and TBH, together with citric acid and, perhaps, sodium erythorbate and ascorbate or alpha-tocopherol and ascorbic acid.

The thorough washing that is suggested in the IAFMM Technical Report No.1 entitled "Potential Food Products from Industrial Fish" should help to extend the induction period before oxidation and rancidity increase relatively rapidly. Mince can be cooked and steam stripped without affecting flavour or protein quality. For cooked and pressed mince the prospects of both short term and long term protection against oxidation are considerably better than for raw mince, as it has less oil and less water.

Storage of minces in the frozen state should be at the lowest available temperature, e.g. below minus thirty degrees centigrade. Storage of salted minces at atmospheric temperatures should be in the coolest, darkest place available.

The most reliable and sensitive test for rancidity is by smell and taste.

ZUSAMMENFASSUNG

In den letzten 20 Jahren wurden beträchtliche Fortschritte im Verständnis der chemischen Vorgänge bei der Oxydation und des Ranzigwerdens der Antioxidans-Aktivität gemacht. Diese Entwicklungen kommen zur Besprechung, aber es wird gefolgert, dass noch bedeutend weitere fundamentale Forschung zu treiben sei, besonders im Zusammenhang mit spezifischen Reaktionen, die in verschiedenen Nahrungsarten vorsichgehen, besonders im Bezug auf Farce aus verschiedenen Industrie-Fischen, über die sehr wenige Versuche und kaum irgendwelche Forschung zu Bericht gekommen sind.

Keine der bekannten Antioxidans-Behandlungen kann sich günstig vergleichen lassen mit dem Schutz gegen Oxydation und Ranzigwerden, der durch hermetisches Abschliessen gegen Sauerstoff-Zugang geboten wird. Für sehr lange Lagerzeiten von Rohfisch oder gekochter und gepresster Farce aus Fettfisch, preserviert durch Salzen oder Frieren, ist jedoch der einzige zuverlässige Schutz gegen Ranzigwerden das Konservieren in Dosen oder Packen in heiss versiegelter Plastik-Folie, nicht unbedingt mit Vakuum. Z.B. würden 50 kg Säcke aus 0.2 mm dicker heissversiegelter Folie und für die Tropen hermetisch verschlossene Trommeln angemessen sein. Die kleinen Grössen von Plastik-Packungen können in den grösseren Behältern gelagert und transportiert werden, bis sie vermarktet werden und dann innerhalb einiger Monate verbraucht werden müssen.

Vielversprechende langzeitige Erfolge sind mit Antioxidantien bei anderen Produkten erreicht worden. Bei der Anwendung von hermetischem Packen für Fischfarcen im Anfangsstadium scheint zufriedenstellendes Lagern solcher Fischfarcen in bekannten synergistischen Mischungen möglich zu sein. Hafermehl und/oder Kräuter und/oder Gewürze und/oder Zitronenöl sollten den Fisch-Farcen beigemischt werden, sofern dies mit dem Endgebrauch des Produktes in Übereinstimmung gebracht werden kann.

Für längeres Lagern von ein paar Monaten, z.B. nach dem Öffnen der grossen hermetisch verschlossenen Packungen, scheint die Aussicht auf erfolgreichen Schutz gegen Oxydation sehr ermutigend zu sein, besonders im Falle gekochter und gepresster Farcen. Die meist versprechenden Antioxidans-Mischungen scheinen EQ und TBH zu sein, in Verbindung mit Zitronensäure und vielleicht noch Natrium-Erythorbat und Askorbat oder Alpha-Tokopherol und Askorbinsäure.

Das gründliche Waschen, das in dem technischen Report Nr. I der IAFMM unter dem Titel "Der Industriefisch als Möglichkeit von Nahrungsmittelprodukten" vorgeschlagen wird, dürfte dazu beitragen, die Induktionszeit zu verlängern, ehe die Oxydation und Ranzigkeit anfängt, verhältnismässig rasch hochzuschnellen. Die Farce kann gekocht und dampfbehandelt werden, ohne dass der Geschmack und die

Proteinqualität beeinflusst werden. Für gekochte und gepresste Farcen sind die Aussichten auf kurzen und langzeitigen Schutz gegen Oxydation besser als für rohe Farce, da sie weniger Öl und Wasser enthalten.

Lagerung von Farcen im gefroerenen Zustand sollte bei der niedrigsten Temperatur geschehen, die möglich ist, d.h. unter 30 °C. Die Lagerung der gesalzenen Farce bei atmosphärischer Temperatur muss am kühlsten, dunkelsten Ort, den man finden kann, vorgenommen werden.

Der zuverlässigste und empfindlichste Test für Ranzigkeit ist Geruch und Geschmack.

RESUMEN

Durante los ultimos veinte anos se ha avanzado mucho en cuanto a la comprension del proceso quimico de oxidacion y ranciedad, y la actividad anti-oxidante. Se discuten estos desarrollos, pero se llega a la conclusion de que aun hay que realizar considerables investigaciones adicionales, especialmente relacionadas con la reaccion especifica experimentada en diferentes alimentos y particularmente en preparados molidos de diferentes peces pelagicos grasos, sobre los cuales se sabe de muy pocas pruebas llevadas a cabo y casi ninguna investigacion.

Ningun tratamiento anti-oxidante conocido puede compararse favorablemente con la proteccion contra oxidacion y ranciedad lograda por sellaje hermetico para excluir contacto con el oxigeno. Para almacenaje a largo plazo de preparado molido crudo o cocinado y prensado a base de pescado graso, ya sea preservado a base de sal o por congelado, la unica proteccion de garantia contra la ranciedad se logra por enlatado o empaquetado en plastico de sellaje hermetico - no necesariamente sellaje al vacio. Por ejemplo, seria apropiado el embalaje en bolsas de 50 kgs selladas por calor, de 0,22 mm de espesor de envoltura, o en cilindros especialmente sellados estancos para los tropicos. Los pequenos paquetes de plastico para venta al por menor pueden ser alamcenados y transportados en contenedores mayores hasta que se marqueticen para utilizacion en unos meses.

Se han obtenido prometadores resultados a largo plazo con anti-oxidantes para otros productos. Mientras que se utiliza embalaje hermetico para los preparados molidos en las fases iniciales, parece ser posible obtener un grado de almacenaje satisfactorio con tales preparados de pescado molido utilizando mezclas sinergistas. Siempre que resulte compatible con la aplicacion del producto, se puede usar con los molidos de pescado, harina de avena, y/o hierbas, y/o especias, y/o aceita de limon.

Para almacenaje durante solo unos meses, p.ej.: despues de abrir paquetes (grandes) hermeticamente sellados, las posibilidades de proteccion satisfactoria contra la oxidacion son mas prometedoras, especialmente en el caso de molidos de pescado cocido o prensado. Entre las aparentemente mejores mezclas anti-oxidantes figura EQ y TBH, junto con acido citrico y, quizas, eritorbato y ascorbato de sodio o alfa-tocoferol y acido ascorbico.

El concienzudo lavado sugerido en el Informe Tecnico No. 1 de la IAFMM, titulado "Productos Alimenticios Potenciales del Pescado Industrial", debiera contribuir a extender el periodo de induccion antes de que la oxidacion y la ranciedad aumenten con relativa rapidez. El molido puede ser cocinado y limpiado en vapor sin afectar la calidad o el contenido proteinico de este. Para los preparados molidos cocidos y

prensados, las perspectivas de proteccion contra oxidacion a corto y a largo plazo son aun mejores que para los molidos crudos, ya que poseen menos aceite y menos agua

El almancenaje de preparados molidos en congelado debiera hacerse a la temperatura mas baja disponible, o sea: a menos de - 30°C. El almacenaje de molidos salados a temperaturas atmosfericas debiera tener lugar en el sitio mas oscuro y fresco posible.

La prueba mas fiable y sensible de ranciedad es por medio de olfato y tacto.

ABBREVIATIONS

AOM.	Active oxygen method of measuring oxidation.
BHA.	Butylated Hydroxyanisole or 2 and 3 isomers of tertiary butyl -4- hydroxyanisole.
BHT.	Butylated Hydroxytoluene or 2,6 - ditertiary butyl -4- methyl phenol.
EDTA.	Calcium disodium ethylenediamine - tetra acetic acid and Disodium ethylenediamine tetra acetic acid.
EQ.	Ethoxyquin.
EQN.	Ethoxyquin Nitroxide.
OAR.	Rate of oxygen absorption.
PG.	Propyl gallate (n-propyl ester of gallic acid).
QS.	Quantum Suffucit - as much as suffices.
TBA.	Thiobarbituric Acid.
TBHP.	2, 4, 5 - Trihydroxybutyrophenol.
TBHQ.	Mono tertiary butyhydroquinone.

1. INTRODUCTION

The most promising food products that can be made on a large economic scale from small fatty industrial fish species are based on minced or finely milled fish flesh, either raw or after cooking and pressing.

One of the major problems connected with this potential development is that of oxidation of the residual oil in the flesh and the development of rancidity during transport and storage.

The present report deals with the various methods for protection of minced fish flesh, made from pelagic oily fish, against rancidity, and not only with the role of antioxidants alone in this process.

The major portion of marine oil is unsaturated. The oils are triglycerides (fatty acid tri-esters) of glycerol. They are not readily soluble in water. Only about 15% to 20% of the oil (mainly palmitic) is saturated. About 40% to 60% is monoenic, and 20% to 35% is polyenoic. Monoenoic and polyenoic C20 and C22 fatty acids are characteristic of fish oil.

Of the polyenoic fatty acids, the pentaenoic and hexaenoic are the ones that oxidise most rapidly. The first oxidation products are hydroperoxide groups formed by the breakdown of fat molecules to free radicals, and the process becomes a chain reaction. The oxidation of oils is catalysed by its own reaction products (unstable free radicals, hydroperoxides, peroxides, etc.). It is thus necessary to add antioxidants before oxidation has really got under way.

These primary oxidation products destroy vitamin E and vitamin A which are readily oxidisable. The hydroperoxides slowly decompose, even at low temperatures. At very low temperatures, both the rate of formation of peroxides and the rate of breakdown are decreased but the rate of breakdown of peroxides is more subject to temperature than the rate of formation and, therefore, at very low temperatures peroxide values can rise to high figures.

The breakdown products of peroxides, by further oxidation, are aldehydes, ketones and acids which contribute to the off-flavours.

Incidentally, oxidation of oil as measured, for instance, by the rate of oxygen absorption is not necessarily synonymous with rancidity, as some oxidation products do not have a smell, but (for fish oils generally) it can be assumed that the higher the oxygen absorption the higher is the degree of rancidity.

The oils contained in small pelagic fishes are highly unsaturated, containing considerable pentaenes and hexaenes, and are rapidly oxidised in the presence of air.

These oils are amongst the most readily oxidised edible oils and present greater problems than the oils in other foods. Mincing alone can double the TBA number and ideally, this should be done under nitrogen or with the exclusion of air. After mincing the flesh, the oil is much more readily oxidised than in fillets or whole fish. The rate of oxidation is faster in minces and fish blocks than when reformed or used as replacers in reformed meat, and is least of all in salami which have an outer covering which restricts the ingress of oxygen.

During the past 30 years or so, there has been considerable progress in understanding the mechanisms of oxidation and rancidification of oil and the means of reducing the rate of rancidification of many products by means of antioxidants. Unfortunately, only little work has been done with fish, let alone mince made from oily fish.

The effectiveness of an antioxidant depends upon the composition of the food to which it is added, and a considerable amount of experimentation remains to be done specifically with raw (oily) fish mince and separately with cooked and pressed mince.

2. REMOVAL OF LIPIDS

Complete removal of the lipids (phospholipids as well as tri-esters) by means of a polar solvent, e.g. alcohol, is very expensive due to the solubility of water in alcohol and its dilution, and the consequent high cost of fractionation and recovery of the solvent. Moreover, the solubility of lipids in alcohol has a steep temperature gradient and the alcohol would have to be heated to be effective. The raw mince would be coagulated, and the functional properties would be impaired.

Indeed, the result would be a Type A (dehydrated) product.

2.1 Reduction of lipid content

This could be achieved by a solvent that is insoluble in water, e.g. hexane, but solvent stripping and recovery, e.g. under vacuum, would be expensive. Moreover, the lipids remaining in the mince are more liable to off-odours and flavours than those which are removed.

3. REPLACEMENT OF LIPIDS

Many years ago, I replaced the fish lipids by introducing successive amounts of (more) stable vegetable oil and pressing after each addition, and this greatly improved the flavour and stability, but the costs were high, particularly as the oil recovered after each pressing was of inferior quality and could not be separated into fish oil and vegetable oil fractions. The addition of gelatine or seaweed extracts to the mince as oxygen barriers also proved very expensive and the tests were abandoned.

4. HERMETIC SEALING

Fish that is canned is not subject to rancidification owing to the absence of oxygen in the can. Comminuted flesh that is preserved by salting or freezing presents problems unless it is hermetically sealed e.g. in cans or in other oxygen-proof packaging, e.g. thickwalled (0.22 mm) heat sealed plastic bags.

It may be mentioned that in experimental work with fish meal, no oxidation occurred when the oxygen content in heat sealed tuck-in valved bags was reduced to a value below 2% oxygen by autoxidation of the fish meal itself. Closing of the bags by stitching was unsatisfactory due to air leakage through the stitch holes. A slight amount of oxidation does not lead to detectable rancidity.

Mild rancidity does not usually have an after taste but severe rancidification does.

Undesirable flavours (e.g.soapy) flavours are also imparted to (unfresh) fish (and other products) by other than oxidative processes, e.g. by free fatty acids especially those that have 14 or less carbon atoms and have lower boiling points and are more soluble in water.

Plastic materials are all permeable to a lesser or greater degree to gases such as oxygen, carbon dioxide, nitrogen and to water vapour. It should also be borne in mind that ultra-violet light and some parts of the visible spectrum accelerate oxidation.

The plastic should be of a suitable type which will prevent the entry of light. It must also be of a type that will not taint the product, e.g. the residual styrene monomer should be kept as low as possible. Moreover, some pigments are toxic and must be avoided. Polystyrene is commonly chosen for packing fatty products.

5. GAS PACKING

The packing of the product in an inert gas, or vacuum packing, are sophisticated and expensive but unnecessary in my experience. As long as the container is filled to its maximum capacity and it is hermetically sealed, (e.g. in tins) or in suitable plastic containers, e.g. thickwalled polystyrene bags that are heat sealed, the product gas packs itself. The oxygen in the container is used up in oxidising some of the oil in the product and no further oxidation can occur, even during very prolonged storage. The degree of rancidity, if any, so produced is below the threshold of detection.

Protection is required after opening large containers if the product is not used immediately.

In this connection, it should be noted that thorough washing of the minces assists in slowing down oxidation and rancidity by washing away oxidation products and blood (haemcompounds containing heavy metals, e.g. iron and copper). The use of citric acid in the washwater would be advantageous in that it would chelate the remaining heavy metals, e.g. iron and copper and reduce pro-oxidant activity.

6. EDIBLE COVERINGS

Comminuted fish that has been reformed, with or without additions, into cakes, blocks, bites, fingers, etc. can be protected against the ingress of oxygen to a great extent by means of edible coverings such as gelatine which is very impermeable to oxygen, or seaweed extracts, e.g. alginates. The addition of an antioxidant or oxygen scavenger to the covering or "glaze" would afford further protection.

The coating of reformed products is best done by dipping the units in a warm strong gelatine solution with glycerine or plasticiser which will set in a thick layer on cooling.

7. FACTORS AFFECTING OXIDATION

All natural products, including fish, contain pro-oxidants and antioxidants and the rate of oxidation depends on the interaction of a number of components in the product such as lipoxidase enzymes, haematin compounds in the haemaglobin, iron, copper, zinc, tin, calcium etc. even when they occur as trace elements. free radicals, etc. all of which accelerate oxidative deterioration.

Fish material has relatively high contents of copper and iron. For instance, fish meal may have a copper content of the order 5 ppm and iron, e.g 250 ppm. most of the latter coming from the processing plant. One wonders whether the few isolated cases of failure of EQ to protect fish meal are related to excessive iron or copper in the meal, and whether the effectiveness of EQ generally could be improved by using it with citric acid.

Haeme catalysis is generally regarded as perhaps the most important single factor in the oxidation of lipids in foods, due to the iron being present in the ferric state rather than in the ferrous state. The acceleration of oxidation by salt is probably due to impurities and particularly heavy metals. Incidentally, trace metals accelerate both the initial oxidation and the decomposition of peroxides.

In the manufacture of salted raw mince or cooked, pressed and salted mince it is essential to ensure that the salt is of the highest quality and as free as possible of heavy metals, especially iron and copper. Moreover, the salt should be sterilised by steaming and guaranteed free from halophilic bacteria, if it is used for producing salted mince for storage at room temperature.

Tocopherols, lecithin, some natural aromatic phenols and amines, organic acids (which often act as synergists) such as citric, acetic, oxalic, tartaric, malic, etc. all retard oxidation. Alpha-tocopherol, the major natural antioxidant, is an efficient antioxidant especially in synergism with BHA, but it antagonises ethoxyquin. Phospholipids such as lecithin and cephalins can act synergistically with added antioxidants.

The oil quality of the fish is of considerable importance in regard to rate and degree of oxidation and this depends on the fish species, time of season etc. It has been shown that the fat composition of the food consumed by fish can influence the fatty acid distribution in the fish body oil.

At the commencement of oxidation there is an induction period during which time the oxidation of the oil is slow, after which the rate of absorption of oxygen as a result of oxidation accelerates, resulting in the development of peroxides and their breakdown products, e.g. non-volatile and volatile carbonyl compounds and other high molecular weight compounds.

The initial period of low increase of oxidation rate (induction period) is decreased by an increasing temperature, by heavy metals, by an oxygen atmosphere vs. air, by light, by the presence of peroxides and other sources of free radicals.

The primary products of oxidation, namely, hydro-peroxides, hardly cause any odour at all but on further oxidation to saturated and unsaturated aldehydes, ketones, and acids the volatile carbonyl compounds cause fishy odours and in advanced oxidation they cause rancid odours and flavours. The non-volatile, unsaturated carbonyl compounds are precursors of volatile carbonyls, and on oxidation are also the cause of odours and flavours.

Oils can be deodorised, i.e. these volatile carbonyl compounds and peroxides can be removed by steam distillation and this process also improves the stability of the oils. Reactions between carbonyl compounds and volatile nitrogenous bases, such as ammonia, are thought to cause brown discoloration of fish flesh. At any rate, oxidation is known to lead to the development of brown (rust) discoloration.

The "toxicity" of oxidised fish lipids has been claimed to be due to free radicals arising from the decomposition of peroxides (and also due to polymers formed during heating) but these products are present in such small quantities that there is no evidence of toxicity of oxidation products of fish lipids in practice.

Oxidised lipids not only lead to the destruction of vitamin E and vitamin A, but the carbonyl compounds react with amino groups with consequent loss of protein quality.

8. HEATING

When producing cooked and pressed mince the peroxides and volatile carbonyls can be removed by steam stripping. By cooking the mince for an hour or so or by heating it to some other temperature for a suitable time, the product can be stabilised against oxidation for an appreciable time.

Many years ago, by cooking fish meal for some time I hoped to inactivate the pro-oxidants and, in fact, the fish meal was stabilised for several weeks. What this is due to is not known. It is suggested that this aspect be investigated with cooked and pressed mince.

In any case, after washing and heat treatment, the amount of antioxidant that would be required for stabilising the cooked and pressed mince would probably be reduced considerably.

9. ANTIOXIDANTS AND SYNERGISTS

Antioxidants are substances which inhibit the rate of reaction of the oil with oxygen. They react with the original free radicals resulting from primary oxidation and interrupt the oxidation chain reaction which would otherwise occur, by binding the radicals which are then not free to react and form new radicals and propogate the oxidation process. Oxidation is thus retarded until the antioxidant is used up. Oxygen scavenging substances are not generally classed as antioxidants.

Synergists are substances which are not necessarily good antioxidants on their own but, when working in combination with other antioxidants, trigger off a combined antioxidant potential which is greater than the sum of the two antioxidants acting on their own. Synergism is not yet completely understood.

In fish lipids, for instance, phospholipids are synergistic with some added antioxidants. Citric acid acts synergistically with some antioxidants and this effect is greater than its effect of chelating iron and copper.

A great deal of research work remains to be done even with well known and tried antioxidants. As regards raw minced fish and cooked and pressed mince, very little research work seems to have been done, even in recent years. Known antioxidants have been used in practice simply because they are effective to some degree, but little research seems to have been done on the specific effectiveness of antioxidants in minced fish, and almost none on minced oily fish and cooked presscake flesh made from oily fish. Antioxidants which may be powerful in one substance may not be so in others; the effectiveness of antioxidants depends on the composition of the product to which it is added.

Thus although a large number of antioxidant trials have been made in connection with various foods and under different conditions of temperature, including cooking, baking and frying temperatures and of storing, much fundamental work is needed for further elucidation of the mode of activity of antioxidants in specific foods and particularly fish, and of the role and mode of action of synergism.

Although some of the antioxidants in use today are pigmented (e.g. dark) and have strong and unpleasant odours and flavours, and are, in fact, toxic, these adverse qualities must be and are, absent when these substances are used in the very small approved amounts in foods. Any undesirable change in colour should not occur. The antioxidants should be liquid or, at any rate, readily soluble in oil and easy to apply. Solid antioxidants should be dissolved in a carrier (e.g. vegetable oil, propylene glycol, alcohol) before addition. When used at, e.g. 0.02%, and when added to several times its weight of oil the total increase in oil of the product to which it is added is only very small.

The antioxidants should preferably not be readily soluble in water, as the objective is to incorporate the antioxidant in the lipid fraction without dilution. The last named requirement is of less importance in cooked and pressed mince than in raw mince, as the former contains much less water. Some antioxidants, e.g. PG, form blue-black iron gallates when water is present.

As fish is usually cooked before it is eaten, it is preferable to use an antioxidant that is relatively stable and active under normal cooking (frying, baking) conditions.

The antioxidant (with or without added synergist, e.g. citric acid in the case of minced fish) must be sufficiently effective to be worth the cost of the material and the cost of incorporation.

9.1. Application of Antioxidant

The antioxidant must be added immediately at manufacture of the product, before oxidation has commenced, to be effective. Uniform distribution is essential.

For uniform distribution, the antioxidant (and synergist) should be added as a fine spray, as the fish material is conveyed through the spray chamber in a relatively thin and turbulent layer (as is presently done with ethoxyquin in fish meal plants); however, as the cooked and pressed mince, and particularly the raw mince, is much more moist than fish meal, and because it is essential to treat every particle to avoid off-flavours, the problem of uniform distribution is greater than that for the treatment of fish meal.

It is suggested that the spray chamber should be much larger, e.g. two or three metres long and that vigorous turbulence be created as the material passes through it.

Even better distribution would be obtained by building a proper "dense fog" chamber rather than a spray chamber and passing the material with turbulence through it. A fog chamber was used for oiling trays to avoid sticking of dehydrated vegetables during World War II and the trays could be passed through the fog chamber at considerable speed.

Good exposure of the minces to the fog could be obtained by high speed screw motion with steep flights for slow movement through the fog chamber but vigorous movement inside it, or by providing broad shaker screens or shelves, preferably with provision for movement of the material from one belt to the next below it within the fog chamber, or by allowing the mince to fall through a vertical fog chamber, using e.g. a spinning disc to "fluff" and scatter the particles as in a spray drying tower.

Another more expensive but perhaps better alternative is to pass the fish material through an avalanching (cascading) rotary drum, constructed internally like a fish meal dryer, into which a dense fog of antioxidant is continually atomised.

9.2. Antioxidants in Use.

Phenolic antioxidants are generally active in animal fats, but less so in vegetable oils.

In practice, opinions vary as to the best antioxidant for a specific food and considerable contradiction is found in the literature. It is not possible to recommend the best available antioxidant or combination specifically for the products in question, namely, raw mince and cooked and pressed mince made from oily fish - and particularly for well-washed varieties of these commodities, either salted or frozen. At this stage, no more can be done than to suggest that certain antioxidants or combinations appear more promising than others for trial and possible use.

It is doubtful, however, whether any known antioxidant or combination, when used in the amounts that are legally permitted in foods, will protect the minces against detectable rancidity for very long periods. It does, however, seem possible to select antioxidants which will protect fish minces for several months when added before freezing, especially at low storage temperatures, e.g. below - 30°C, and for somewhat shorter periods for minces that are salted and kept at atmospheric temperature. The ideal for long term storage is to use hermetically sealed packaging, with antioxidant added to protect the products for a few months after opening.

As cooked, pressed minces have less oil than raw minces and as the moisture content is lower it seems likely that these can be kept in rancid-free condition for longer periods than the raw minces. Packaging, storage and transport are also less expensive.

If the minces are to be stored after incorporation in food formulations e.g. in sauces, or in reformed products, the antioxidant and pro-oxidant properties of the added materials will have a bearing on the ultimate result.

Many natural products contain antioxidants, e.g. oat flour and other cereal flours, some vegetable oils (palm, Sesame, wheatgerm oil) and especially citrus oils consisting of terpenes (over 90%) - lemon oil is cheaper than orange oil and improves the flavour of fish, sugar, resin guaiac, citric acid, tartaric acid, Vitamin C (ascorbic acid), sage, rosemary and other herbs and spices and odourless and tasteless extracts made from these, smoke constituents, phosphatides, polyphosphates, and especially some complex organic phenols and aromatic aldehydes, but not simple phenols or aniline. Rosemary and sage or other herbs would also have flavour and masking qualities in the minces.

The odourless and tasteless extracts of sage and rosemary appear to be suitable as antioxidants for use in potato chips and in soya bean oil. It is not known how they act in fish material. But sage and rosemary in the natural state do improve fish odour and flavour in storage even when added uniformly in small, almost undetectable amounts. Oat flour is known to improve the keeping quality of fish.

Most antioxidants in practice have trade names, e.g. Ionol (BHT), Tenox solutions (BHA BHT, TBHQ, PG, either singly or in mixtures together with citric acid and solvents), Santoquin (EQ) Freezegard (sodium erythorbate, polyphosphates and salt), Ronoxan (Tocopherol and ascorbic acid).

9.2.1. EQ Ethoxyquin

This potent antioxidant is widely used for feeds and apparently now also for foods. It is readily oxidised to a stable free radical which is an even more potent and superior antioxidant. As it is used in the Fish Meal Industry, with good effect, it may be possible that it could be used with good effect in fish minces (including Surimi) when used within the legally permitted limits, and trials seem to be indicated. The reason for the long-term potency in fish meal (permitting only very low level oxidation for years) is not yet understood. It is known that when ethoxyquin is oxidised to EQN. to which it is readily oxidised to form a stable free radical, its potency as an antioxidant in unsaturated lipids is somewhat increased, but it is doubtful whether this is the explanation for its long term effect specifically in fish meal. Very little seems to be known of the fate of other antioxidants, in general, as they become used up in action but they generally become "spent" and inactive.

9.2.2. Proline Nitroxides

Proline nitroxide is a relatively stable free radical with a yellow colour and a sharp odour. It dissolves in water but hardly in oil. It has strong antioxidant activity in unsaturated lipids. Stable nitroxides are generally very effective antioxidants especially in, e.g. squalene (ethylene unsaturated lipid) but are less so in methylated interrupted unsaturated lipids such as fish oils. They have low toxicity. However, they are not in general use, perhaps partly due to the high cost of production?

9.2.3. Ascorbic Acid, Isoascorbic Acid and Citric Acid

These products are white or colourless, and tasteless to slightly acid. Ascorbic and isoascorbic acid are often used for other oxidative changes than rancidity. They are oxygen scavengers in the food industry.

Ascorbic and citric acids are, however, also antioxidants in their own right, and combined with smoke (e.g. 0.1% of each) ascorbic acid acts synergistically and is relatively powerful. This combination might be considered if smoked fish minces are envisaged. Ascorbic and citric acids are soluble in water and not in oil, and are not of much use without phenolic antioxidants. Nevertheless, by themselves they have been reported as having antioxidant effect with herring fillets.

Citric (and phosphoric) acids have antioxidant properties with vegetable oils but are not usually very effective with animal fats.

A commercial product contains d-alpha tocopherol 5%, lecithin approx. 7% and ascorbyl palmitate 25%. It is a brownish paste with a slight odour and taste but does not affect the taste of oils when used in permitted amounts.

9.2.4. BHA and BHT

BHA is a white or yellowish waxy solid with a phenolic odour. It must be protected from light. It is practically insoluble in water but is soluble in oil and in propylene glycol. BHA and BHT resist mildly alkaline conditions (though phenolic antioxidants are generally acidic and do not act well in alkaline media) - but are distilled by steam. They are not very potent antioxidants by themselves but act synergistically with each other and with other phenolic antioxidants and with citric acid etc. - as do other phenolic antioxidants. BHA also acts with dithiopropionic acid (e.g. 0.01% of each). Numerous antioxidant mixtures have been developed with BHA, BHT, gallates and citric acid; BHA is also used in combination with gallic or phosphoric acid.

BHA and other phenolic antioxidants, such as BHT and ethyl gallate are not very effective in protecting frozen fish from oxidation. In fact, antioxidants, in general, have not proved very effective with frozen fish. Nevertheless, BHA is widely used for frozen fish but its use is almost entirely prohibited in Japan. A claim is made in a recent patent that BHA protects fish against oxidation at room temperature for long periods but, in my opinion, this would not hold with pilchards or anchovies.

BHA and BHT are used in vegetable products, confectionery, margarine, soft drinks, etc. but have proved inferior to EQ in fish meal.

The presence of considerable alkaline ions e.g. sodium and potassium, could react with BHA to cause pink discoloration. This could happen with heavily salted fish. Both BHA and BHT produce slight, but not serious, discoloration in the presence of iron.

BHT is a white flaky solid, also with a phenolic odour; it imparts a phenolic odour to fat when used at 0.02%. It is insoluble in water, and also in propylene glycol. Vegetable oil (peanut) or alcohol is used as solvent. It is less expensive than BHA.

Both BHA and BHT are used extensively and have proved effective for many purposes.

9.2.5. TBHQ

This antioxidant is a whitish crystalline powder which is soluble in propylene glycol, alcohol and in food fats and oils but not in water. It is slightly less volatile than BHA and is better than BHA, BHT and Gallates for unsaturated oils, and survives frying and baking temperatures. It is eminently suitable for unsaturated marine oils such as whale, herring, mackerel etc. It does not discolour in the presence of iron.

In combination with citric acid (0.02%) it stabilised herring oil for 14 months and had the advantage of retarding the formation of carbonyl compounds (rancid odour) and other secondary oxidation products. It is claimed to be excellent for retarding the absorption of oxygen by unsaturated lipids in fish fillets and in minced fish. The mixture has given good results for 8 weeks in the storage of frozen whiting mince.

TBHQ (0.02%) has been found to be similar in effectiveness to EQ during the first two months of storage of fish, better at 4 months, and inferior after 6 to 8 months storage. The "index" of effectiveness used was iodine value.

Generally, the oxidation products of antioxidants diminish their antioxidant properties but in the case of TBHQ, as for EQ, the antioxidant properties are enhanced.

TBHQ is used in combination with citric acid which acts synergistically. For instance, a mixture on the market contains 11% TBHQ, 36% of citric acid in 53% ethanol. Another contains 20% TBHQ and 10% citric acid with 70% propylene glycol. These mixtures, which are proprietary brands, or other combinations, seem worth trying with minces made from pelagic fish. TBHQ is, however, expensive, e.g. more than four times as expensive as ethoxyquin, about one-third more than BHA and more than six times as expensive as BHT which is the cheapest antioxidant of all.

TBHQ may be used with BHA and/or BHT at a maximum combined concentration of 0.02% on the weight of the oil in the mince (or other product). The use of TBHQ with PG is apparently not permitted in the USA.

9.2.6. EDTA

The salts are white powders or crystals with a faintly saline smell. They dissolve freely in water but poorly in oil. Just as citric acid, it is often used for inactivating iron, copper and other metals in fish. Fish dipped in 1% EDTA solution for one minute extends the storage life of fish considerably, e.g. to 14 days on ice.

9.2.7. Gallates

Esters of gallic acid are white to greyish solids, and are odourless but slightly astringent to the palate. They can cause violet discoloration with iron, and citric acid should be used with the gallates to sequester the iron.

Gallic acid, propyl gallate and other gallates, e.g. octyl, decyl and dodecyl gallates are good antioxidants and are used, e.g. for margarine and fats. Propyl gallate is often more effective than BHT and BHA. Gallates are insoluble in water, but dissolve in alcohol, oils and propylene glycol. They decompose at the high temperatures used in frying fish and other foods. Propyl gallate with citric acid proved effective in an 8 week storage test with minced whiting flesh. An effective antioxidant is also obtained when PG is used in combination with BHA, BHT and citric acid. The maximum permitted PG, or PG plus other antioxidants, is generally 0.02% of the oil in the fish or other food. It should be noted that phenolic antioxidants (BHA,BHT,PG) are slightly acidic; whereas PG is inactivated in alkaline media, BHA and BHT retain their effectiveness in slightly alkaline media.

9.2.8. Sodium Erythorbate

This antioxidant "proved effective" in a storage test with minced fish. It gave equal results to sodium ascorbate, but is cheaper. Sodium erythorbate is more of an oxygen scavenger than a true antioxidant. Freezgard (FP-88E), a commercial preparation, containing sodium erythorbate, d-isoascorbate, polyphosphates and sodium chloride, has apparently proved highly effective with suckers, but according to another worker, not more so that sodium erythorbate with ascorbate, with minced fish.

9.2.9. Mixed Tocopherols (Precursors of Vitamin E)

These concentrated oils are made by vacuum distillation of vegetable oils, and have a strength of at least 24% of tocopherols, of which about half is alpha-tocopherol. This latter has a slightly yellow colour and is (nearly) odourless, but the mixed tocopherols have a reddish/brownish colour. They darken in air and light.

This major natural antioxidant has, in some experiments, been less potent than BHA, BHT, etc. but acts synergistically with BHA; but with chicken alpha-tocopherol acetate proved more effective than BHT.

9.3. Antioxidant Manufacturers

Many chemical manufacturers produce antioxidants. Examples of large Chemical Organisations and of their products are, for instance :-

Monsanto (Santoquin :EQ)
Eastman Kodak Chemicals (Tenox : Mixtures containing one or more of the following: BHA, BHT, TBHQ, PG and citric acid in a solvent carrier.

Shell (Ionol: BHA)
May & Baker (Embanox : TBHQ)
Naarden, Holland (Gallates)
Roche (Ronoxan : Vitamin E, Ascorbyl palmitate, d.l. alphatocopherol and lecithin.
Kemin Industries (Endox : BHT, BHA and TBHQ plus solvent).

9.4. Government Regulations

Different countries have different regulations governing antioxidants in foods, and the maximum limits vary. Users must, therefore, consult the Regulations of the country in question.

As examples, the USA usually permits (mostly to a maximum of 0.02%) the following antioxidants based on the weight of the fat in the food product :-

EQ, BHA, BHT, PG, TBHQ, Gum Quaiac, Lecithin, mixed tocopherols, Vitamin E. TBHP and glycine.

Certain restrictions are applied to some of these antioxidants.

Other antioxidants are also allowed in certain foods in specified maximum quantities.

BHA, BHT and PG are, however, the most widely used antioxidants.

Dutch Regulations permit ascorbyl palmitate (0.3% on oil), natural and synthetic tocopherols (0.5%) gallates and/or BHA and/or BHT (0.01% total) citric acid (q/s).

TBHQ, BHA, BHT and PG are permitted in Australia, Brazil, Peru and South Africa in the above general amounts. South African Regulations permit resin quaiac (0.1%), tocopherol (0.03%), lecithin (qs), tartaric and ascorbic acid (qs), gallates (0.01%) with or without 0.005% of citric acid, BHA (0.02%) with or without gallates (0.01%) and 0.005% of citric acid or phosphoric acid. EQ is only permitted (3 ppm) on apples and pears.

10. MEASUREMENT OF OXIDATION

There are many methods of measuring the rate of oxidation and rancidification of oils. As regards rancidity itself, the human nose is more sensitive as a detector than most methods, even including the most sophisticated physical and chemical equipment. The nose also represents the most reliable method of detecting off-odours. A good taste panel is, therefore, of prime importance. Although peroxides have no off-taste there is fortunately a fair general relationship between oxidation and off-taste in fish.

The measurement of the rate of oxygen absorption e.g. by means of a flask and manometer or a Warburg apparatus at 50°Celsius or lower, is perhaps the simplest and fastest method for measuring the rate of oxidation. Chemical methods for measuring oxidation include iodine value, peroxide value, TBA (thio barbituric acid) value infra-red and ultra-violet spectroscopy, active oxygen method (AOM), beta carotene protection and, for fish, the rate of decrease of C22:6 fatty acid.

In the active oxygen method (AOM), sometimes called the Swift Stability Test, the rate of formation of peroxides is measured at nearly 100°C (e.g. 97,8°C) while a flow of air is maintained over the oil. The time required for the peroxide number to reach e.g. 20 for animal fats, or e.g. 80 for vegetable fats is measured. These numbers are more or less related to the induction period. The test is simple and relatively accurate but it does not give a reliable index, in my opinion, of the behaviour of the product as a whole when stored under normal conditions.

In the Schaal test the oil is heated to 60°C in air and the peroxide value and taste are measured from time to time for comparative purposes. Peroxide values and TBA values are themselves unstable and are not, to my mind, suitable as test figures. Indeed, the figures rise and then fall, and a given figure may be achieved either on the way up or on the way down. In these methods the oil must be extracted from the fish mince and it is almost impossible to extract the oil without changing it even slightly.

The oxygen absorption method for fish meal has been used by me for many years with success.

To detect rancidity, the aging test is best in my opinion. The mince is stored at about 30°C if salted or dried, or at about - 10°C if intended for frozen storage, in plenty of air, and it is examined by an organoleptic panel for rancidity from time to time.

11. HEALTH ASPECTS

The term "toxicity" is generally used erroneously, without definition, to denote substances that may cause harm if consumed. But many so-called toxic substances are harmless or even beneficial to health if taken in lesser amounts than cause harm. For instance, selenium, arsenic, salt etc. if completely absent from our foods will result in ill health and even death.

Could this be the case with antioxidants? Autoxidation in animal tissue is an important factor in the aging process, and there have been reports of benign physiological action of antioxidants - and even of anti-cancer activity. It does not seem to be known yet whether such products would, or could be made to act beneficially when added to foods, nor whether the highly reactive oil in mince, made from industrial fish, could act beneficially as an oxygen scavenger, even when treated with an antioxidant that becomes inactivated in metabolism.

12. CONCLUSIONS AND RECOMMENDATIONS

1. Until more potent antioxidants are available for indefinite long term storage it is suggested that raw, and cooked and pressed, fish minces intended for freezing or salting, be packaged in large, e.g. 50 kg. heat sealed plastic containers made of solid polystyrene sheet of adequate, e.g. 0.22 mm thickness. The containers must be filled to capacity for minimum air (oxygen) content.

2. For short term storage for several months, e.g. after opening the bags, trials should be made with promising synergistic mixtures which are permitted in terms of Government Regulations, i.e. TBHO with citric acid or EQ or PG with citric acid, or, perhaps, sodium erythorbate with ascorbate or alpha-tocopherol and ascorbic acid.

3. Application should be made to the Authorities for permission to use EQ specifically in minces made from pelagic fish, as these have more reactive lipids than normally found in foods.

4. It is suggested that the effect be studied of adding lemon oil and citric acid (both are natural antioxidants) and/or sage and/or rosemary, and/or oats or the odourless and tasteless extracts therefrom, depending upon end use.

5. It is of vital importance to add antioxidants immediately after manufacture and to ensure absolutely uniform distribution throughout the minces. One of the most frequent causes of failure is lack of uniform distribution of the antioxidant.

6. The simplest and easiest test for oxidation is by the measurement of OAR using, e.g. a flask and manometer, or a Warburg apparatus in which a number of samples can be accommodated at a time; and the easiest and most meaningful test for rancidity in fish mince is by smell and taste of products stored under normal conditions. This should be the main criterion for all tests. An absence of smell does not necessarily mean an absence in taste, and vice versa.

7. Several factors render the stabilisation of cooked and pressed mince easier, and with the use of less antioxidant, than raw mince. A cooking/heating procedure, which does not affect protein quality or the flavour, should be tried for stabilisation.

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