

IAFMM

FISH OIL BULLETIN

international association of fish meal manufacturers

Hoval House, Orchard Parade, Mutton Lane, Potters Bar, Herts. EN6 3AR, England.
Tel: (Potters Bar) 0707 42343/4/5 Telex: 8811909 London.

No 15 September 1982

TECHNICAL REASONS GIVEN BY BUYERS FOR IMPOSING PENALTIES AGAINST FISH OIL PRODUCERS

1. Reasons relating to yield
 - 1.1 High free fatty acid content
 - 1.2 Low refining yield
 - 1.3 High "gum" content
2. Reasons relating to contamination
 - 2.1 High moisture and/or dirt
 - 2.2 Contamination with mineral oil
 - 2.3 Low saponification value/high unsaponifiable matter content
 - 2.4 Soap content
3. Reasons relating to oxidation
 - 3.1 Poor oxidation stability of refined deodorised hydrogenated product
 - 3.2 Colour complaints
 - 3.3 Oil has been overheated
4. Reasons relating to hydrogenation
 - 4.1 Poor hardening performance

1.Reasons relating to yield

1.1. High free fatty acid content

1.1.1 Examples of complaints

FFA out of specification on receipt of oil by buyer.

FFA in specification on receipt but increasing on storage.

1.1.2 Causes

Presence of free water (greater than 0.2%) with or without enzymes, particularly if oil not given a final water wash "polishing" treatment.

Overheating i.e. storage at over 35°C.

1.1.3 Effect

Results in higher losses in the neutralisation stage of refining.

1.1.4 Principally associated with:

1.2 Low refining yield

1.3 High 'gum' content.

2.1 High moisture and/or dirt.

2.5 Soap content

1.1.5 Counter-arguments

Incorrectly sampled by buyer; non representative sample.

Incorrect FFA test; check method and reagents.

Increase in FFA occurred during shipment or during storage in buyer's tanks due to dirty or wet tanks or overheating.

1. Reasons relating to yield

1.2 Low refining yield

1.2.1 Examples of complaints

High American Oil Chemists' Society (AOCS) "Cup" or chromatographic loss or high "Wesson" loss - all these are laboratory methods for determining the refining loss.

Unexpectedly high plant refining loss.

High bleaching earth usage.

1.2.2 Causes

High FFA in oil.

High dirt in oil.

High phosphatides ("gums") in oil.

Dark colour of oil.

Incorrect refining treatment.

1.2.3 Effects

Increased costs.

1.2.4 Principally associated with:

1.1 High free fatty acid content.

1.3 High gum content.

2.1 High dirt content.

3.2 Dark colour.

1.2.5 Counter-arguments

Apart from in the U.S.A. where they are principally used for soyabean and cottonseed oils, the laboratory tests are rarely used as quality control checks on incoming crude oils. They are used more for checking refinery performance. The tests are not easy to perform and do not give good repeatability.

The refining yield is affected by dirt in the buyer's tanks.

The refining process should be varied according to the oil quality. The refiner may not be using the

1.2 Low refining yield

correct process conditions e.g. not using or not using enough degumming acid; not using the correct strength or excess of caustic soda. The refining yield can be improved by using the correct conditions.

For colour see item 3 - Reasons relating to oxidation.

Neutral oil lost in neutralising and deodorising is recovered, at a lower value, in the acid oil by-product. Cost compensation should take this fact into account.

Notes

The refining yield, or more specifically the neutralisation yield is frequently expressed as the Acid Oil Factor (AOF).

$$\text{AOF.} = \frac{\% \text{ loss in neutralising and washing}}{\% \text{ FFA in the crude oil}}$$

The AOF depends on the process used and on the oil quality. Normal AOF figures for fish oil through a continuous refining line are between 1.8 and 2.2.

Note: Losses in the refining process may also be given as the more general Refining Factor (RF).

$$\text{RF.} = \frac{\% \text{ loss in one or more refining stages}}{\% \text{ FFA in the crude oil.}}$$

The RF should always be stated with information on the stages included in the calculation e.g. RF (Neutralising and bleaching)

Normal losses refining fish oil:	Loss
Neutralising and washing:-	2 x FFA%
Bleaching depends on type of earth and filter press:-	1/3rd to 2/3rds of % of earth used
Hydrogenation:-	Nil
Post-hydrogenation refining depends on process (neutralising & bleaching or (bleaching only	1% or 0.5%
Deodorising:-	0.5%

1. Reasons relating to yield

1.3 High gum content

1.3.1 Examples of complaints

Oil frothy or thick (high viscosity) or dirty.

High phosphorus content.

1.3.2 Causes

A high level of phosphatides or protein breakdown products. These compounds can be dissolved in the oil, or as a colloidal suspension or larger dirt particles. Can be reduced by giving the oil a polishing wash. They are the result of enzymic action.

1.3.3 Effects

These compounds act as emulsifying agents and increase losses due to emulsification if the oil is not treated with a water wash and/or phosphoric acid or other degumming agent before neutralisation.

Increase oil losses due to increased sludge in storage tanks.

Give emulsion problems when splitting soapstock with sulphuric acid for the production of "acid oil".

Can produce darkening of oil at high temperatures (>160°C)

1.3.4 Principally associated with:

1.2 Low refining yield.

2.1 High moisture and/or dirt.

1.3.5 Counter-arguments

Contamination with sludge in buyer's storage tank.

Check phosphorus content. Phosphorus is converted to phosphatides by multiplying by 30. There is little information on "normal" levels of phosphatides in fish oils

1.3 High gum content

but in general over 0.5% (~ 150 ppm P) can be taken as a high level and 0.05 to 0.25% (~ 15 to 80 ppm P) as good to average.

Refining process parameters could be improved.

Financial loss should be based on difference between neutral oil and acid oil prices (see 1.2.5.)

2. Reasons relating to contamination

2.1 High moisture and/or dirt

2.1.1 Examples of complaints

As in heading.

2.1.2 Causes

Poor separation in centrifuge.

No polishing water wash.

Contamination during storage or transport.

2.1.3 Effects

High refining losses

General reduction in quality

2.1.4 Principally association with:

1.1 High free fatty acid content.

1.2 Low refining yield

1.3 High gum content

2.1.5 Counter-arguments

Contamination during storage or transport

Non-representative sample

2. Reasons relating to contamination

2.2 Contamination with mineral oil

2.2.1 Example of complaint

As in heading.

2.2.2 Causes

Contamination during storage or transport.

Wax esters mistakenly identified as mineral oil.

2.2.3 Effect

Renders oil unusable for edible purposes.

2.2.4 Principally associated with:

2.3 Low saponifiable value/high unsaponifiable matter content.

2.2.5 Counter-arguments

Check test method - fluorescence under U.V. light may be due to wax esters or other non-toxic oil component. (Only reliable methods known to writer are:-

Leatherhead Food RA method,
Bories and Tulliez, J.Sci.Fd.Agric. 1977, 28, 996-9.
(IAFMM has copies of both methods)

Contamination during transport and storage.

2. Reasons relating to contamination

2.3 Low saponification value/high unsaponifiable matter content

2.3.1 Examples of complaints

As in heading.

Nutritionally harmful.

Contains mineral oil.

Contaminated.

Effect on sale of acid oil.

Will cause high losses or is indicative of poor quality.

2.3.2 Causes

Increased unsaponifiable matter is attributed primarily to an increase of wax esters. The effect is considered to be seasonal and dependent on the diet of the fish.

2.3.3 Effects

The hydrocarbon fraction of the unsaponifiable matter is reported to be virtually completely removed from the oil during deodorisation. The hydrocarbon content is about 10% of the unsaponifiable matter. Higher hydrocarbon contents would therefore result in higher losses, but not significantly so when viewed against the variation in deodoriser loss normally encountered.

It is stated that the high unsap oil results in a reduction in the yield of distilled fatty acids after splitting the acid oil. The tolerable unsap upper limit in this effect is not known. Unconfirmed information has been received that the residual "foots" from the distillation step can be sold for inclusion in animal feed.

2.3.4 Principally associated with

2.2. Contamination with mineral oil.

2.3 Low saponification value/high unsaponifiable matter content

2.3.5 Counter-arguments

Nutrition: Certain fish "oils" with very high wax contents have been found to be harmful when fed in substantial quantities to rats (M. Mori, Japanese Soc. Scientific Fisheries, 1966, 32, (2), 137-145; Y. Hashimoto, "Marine Toxins and Other Bioactive Marine Metabolites", Japan Scientific Societies Press, 1979). Currently there is no evidence of harmful effects on humans from the levels of unsaponifiables found in the common industrial fish oils. It is believed that these levels pass through the body unchanged and without effect.

Mineral oil: This is generally a case of mistaken identity. (See 2.2).

Contamination: The high levels of unsaponifiables are normally due to the diet of the fish.

Losses/quality: There is no evidence of significantly higher losses, of processing trouble or of reduced quality from fresh oil with the levels of unsaponifiables encountered seasonally in the fish currently processed on an industrial scale. From the writer's enquiries most refiners do not check the level of unsaponifiable matter in the oil.

2. Reasons relating to contamination

2.4 Soap content

2.4.1 Examples of complaints

As in heading.

2.4.2 Causes

The refining of the oil or part of it with alkaline materials.

Contamination during transport or storage.

2.4.3 Effects

The soap itself has no effect on refining.

The presence of soap will catalyse the production of fatty acids on storage.

The refining of the oil is carried out at elevated temperatures (60 to 90°C) and results in a reduction in the content of natural antioxidants. During subsequent storage the colour of the oil becomes fixed and oxidation is more rapid than in the crude oil.

2.4.4 Principally associated with:

3. Claims relating to oxidation e.g. high oxidation values, poor flavour stability of the refined deodorised hardened product, poor bleachability.

2.4.5 Counter-arguments

Road tankers or storage tanks may have been cleaned using alkaline agents and not properly rinsed.

Sample bottles not rinsed after cleaning.

The analytical method most commonly used is the Wolff, or titrimetric, method. The test is satisfactory for gross contamination (>100 ppm) but must be carried out scrupulously for lower levels.

2.4 Soap content

The Codex Alimentarius Commission's "Recommended International General Standard for Edible Fats and Oils not covered by individual Codex Standards" Section 5 "Contaminants", 5.3. "Soap Content" sets the maximum permissible level at 0.005% m/m (i.e. 50 ppm).

3. Reasons relating to oxidation

3.1 Poor oxidation stability of refined, deodorised, hydrogenated (RDH) product.

3.1.1 Examples of complaints

Rapid development of off-odours or -flavours in the RDH oil or in the baked product.

Poor stability in oxidation test e.g. A.O.M. (Active Oxygen or Swift Method); Schaal oven test; FIRA-Astell test.

3.1.2 Causes

High level of oxidation in the crude oil as measured by peroxide and anisidine or other such tests.

High levels of trace metals, copper and iron in the crude oil. Can arise during transport and storage.

Contamination of a good crude oil by remnants of poor quality oil in a dirty storage tank.

Poor refining practice e.g. storage at any stage in the refining process for too long and/or too high a temperature. In general the oil should be passed through the refining/hydrogenation process as quickly as possible. If storage is to exceed 12 hours, the liquid fish oil should be cooled to $<40^{\circ}\text{C}$ and the hydrogenated oil to 10°C above its melting point. The RDH oil should be used within 24 hours of deodorisation. For consistency of solids content of the hydrogenated oil it is frequently stored for two weeks. If this is done, the storage should be at low temperature and should follow the post-hardening refining treatment.

3.1.3 Effects

Off-flavours or off-odours develop rapidly in the margarine, shortening or final product (biscuits, cakes) making them unacceptable. The odours in particular are noticeable in a kitchen or bakery where such oils are being used. The long life required of biscuits makes them particularly susceptible to this defect. RDH fish oil is generally not acceptable for frying for this reason.

3.1 Poor oxidation stability of refined deodorised hydrogenated product

3.1.4 Principally associated with

1.1 High FFA content (in the crude oil).

3.2 Poor bleachability/dark colour.

3.3 Overheating of the oil.

4.1 Poor hardening performance.

3.1.5 Counter-arguments

Knowledge of the oxidation values at the time of shipment and on arrival at the buyer's installation.

Knowledge of no trace copper contamination in the extraction plant e.g. from brass or bronze in contact with the oil.

Look for contamination with old oil or copper and iron (rust) or for overheating during transport or storage, including following arrival at the buyer's premises.

Poor refining practice as outlined in 3.1.2.

Note: the refiner should protect the deodorised oil by addition of citric acid; this is not infrequently forgotten or missed out for cost reasons.

The oxidation tests mentioned in 3.1.1. are unreliable due to various problems with the apparatus.

3. Reasons relating to oxidation

3.2 Colour complaints

3.2.1 Examples of complaints

- A. Poor bleachability; dark colour.
- B. Oil darkens during hydrogenation or deodorisation.
Increased refining costs to obtain acceptable colour.

3.2.2 Causes

- A. Colour fixation due to oxidation with particular reference to trace iron content.

High level of pigments in the fresh crude oil.

Overheating ($>50^{\circ}\text{C}$).

- B. High sulphur in conjunction with high (>0.5 ppm) iron or nickel in the hydrogenated oil.

3.2.3 Effects

- A. Use of more and stronger caustic soda solutions and extra and/or more active bleaching earth in refining process, with consequent increase of costs. (See "Extra Effort and Cost....." report 3/4/80, V. Young).

- B. Oil is either rejected and has to be re-refined or can only be used for margarine because of high colour.

3.2.4 Principally associated with:

- 1.1 High FFA content (in crude oil)
- 3.1 Poor oxidation stability of RDH oil.
- 3.3 Overheating of oil.
- 4.1 Poor hardening performance.

3.2.5 Counter-arguments

- A. High colours in otherwise good quality crude oils will be removed during caustic soda refining, bleaching and high temperature (250°C) deodorising.

3.2 Colour complaints

A bleaching and heating test can be carried out on the oil and compared with previous results from oils of known quality.

The problem can be the result of contamination and poor storage conditions or overheating.

B. This problem is normally associated with high nickel content (>0.5 ppm) in combination with traces of sulphur. With correct processing the nickel level after the post-hardening refining treatment will be less than 0.2 ppm, at which level darkening will not occur.

n. **Reasons relating to oxidation.**

3.3 **Oil has been overheated**

3.3.1 **Examples of complaints**

High colour/colour fixed.

Smell of oil not fresh, or burned.

Coefficients of extinction ($E_{1\text{cm}}^{1\%}$ 233 and/or 268nm) are high.

3.3.2 **Causes**

The oil has been accidentally heated to over 50°C in the presence of air and possibly light.

Steam of too high pressure ($>3\text{kg}/\text{cm}^2$) has been used to melt the stearin which settles to the bottom of the tank under cold conditions.

3.3.3 **Effects**

The natural pigments in the oil are degraded to compounds which colour the oil more deeply and are not as readily removed by bleaching clays.

The heat causes isomerisation of the fatty acids producing more conjugated double bonds which are indicated by increases in the coefficient of extinction.

The oil may smell burned.

3.3.4 **Principally associated with:**

3.1 Poor oxidation stability of the RDH oil.

3.2 Poor bleachability; dark colour.

3.3.5 **Counter-arguments**

This problem normally arises during ship transport in cold climates.

It may also occur if heating steam is accidentally left turned on.

3.3 Oil has been overheated

The colour and bleachability of the oil should be checked before despatch, or a reference sample should be stored in a full, screw-capped, brown bottle in a refrigerator so that the tests can be carried out if a complaint is received.

4. Reasons relating to hydrogenation

4.1 Poor hardening performance

4.1.1 Examples of complaints

Excessive hydrogenation time.

Increased hydrogenation catalyst consumption.

High sulphur content in crude oil.

Internal standard refining and hydrogenation test indicates poor oil quality.

4.1.2 Causes

The nickel catalyst used in hydrogenation is "poisoned" (loses its activity) due to the adsorption on to its surface of chemicals containing sulphur or oxidation products or halogens (chlorine, bromine and iodine). The refining process prior to hydrogenation should remove about half of the sulphur compounds and a large proportion of the oxidation products but it has very little effect on the halogen-containing compounds.

4.1.3 Effects

Increased costs. In bad cases a double hydrogenation treatment may be required, the first with "used" catalyst to adsorb the poisons and the second to produce the hydrogenated fat.

4.1.4 Principally associated with:

1.1 High FFA content of the crude oil.

1.3 High gum content.

3.2 Colour complaints.

4.1.5 Counter-arguments

Determine sulphur content of despatched crude oil sample (should be <30 ppm - Modified Baltes Method).

Carry out refining and hydrogenation test. If this cannot be done on the oil extractor's premises there are independent laboratories where the test can be carried out.

4.1 Poor hardening performance

If applicable, point out that other quality parameters are good, thus indicating that there should be no problem with hydrogenation.

The oil may have been contaminated with another old or poor quality oil - fresh oil pumped on top of old oil is a frequent occurrence.

The refining process may be inadequate.

The hydrogenation catalyst may be insufficiently active.

Check the buyer's refining and hydrogenation test procedure. It should include:-

a degumming treatment with phosphoric acid,

at least one neutralisation with strong (4 Normal) caustic soda solution,

efficient washing of the oil to reduce the soap content to <100 ppm,

bleaching with at least 1% of an acid-activated bleaching earth for 30 minutes at 90°C,

filtration followed immediately by

hydrogenation using an active (unused) catalyst.

F.V.K.Young