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CAUSE AND REMEDY

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COLOUR REVERSION OF REFINED PALM OIL: CAUSE AND REMEDY

by
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Refined, bleached and deodorised (RBD) palm oil has a yellowish colour specified as 3 Red maximum in the PORAM Trading Specifications. However, after some time, colour reversion may take place and darkens the oil; this is a common phenomenon not only for palm oil, but for other oils and fats as well. In the case of palm oil, some of the causes - the compounds responsible for the colour reversion - are still unknown and are being investigated (Ooi *et al.*, 1993).

It is a well-known fact that colour development in an oil is very much associated with oxidation that could take place due to exposure to air, presence of pro-oxidant, improper processing and mishandling.

Many importers of palm oil redeodorise their RBD palm oil to further reduce the colour, FFA and oxidised products that have increased slightly during shipping. However and occasionally, the above quality parameters rise significantly even after deodorisation. This suggests that the oil had not been refined properly resulting in poor quality of the refined oil. Unfortunately, the 'symptoms' or the indications of poor quality are not immediately apparent after the oil was first refined. It takes some time for the problem to surface and thus buyers can be misled by the initially high quality of the refined oil.

From the consumer point of view, the darkening of the oil is a sign of poor quality and thus undesirable. On the other hand, refiners relate the darkening of palm oil with improper processing of the oil as the quality of the final product is heavily dependant on how it was processed and the initial quality of the input. These problems are rectifiable and can be effectively prevented along the processing line. With recent advance in processing technology and increased understanding of the physico-chemical properties of palm oil, special quality palm oil with low colour can be produced commercially at a premium price. The colour reversion though not fully understood can be controlled and minimised.

The following discussion describes briefly the physical refining of palm oil and the possible causes for colour instability and their remedy.

Refining of Palm Oil

Crude oils are refined to remove all impurities, such as undesirable odour, flavour and colour but at the same time retaining the beneficial components such as the vitamins and pro vitamins. *Table 1* summarises the impurities contained in palm oil.

Table 1. Impurities in Palm Oil

Hydrolytic	**moisture, dirt, FFA, partial glycerides, enzymes**
Oxidative	**trace metals, oxidation products, pigments, phosphatides**
Catalysts	**compounds containing nitrogen, sulphur, and halogen poisons**
Others	**hydrocarbon, waxes, terpenes, sugars, sterols**

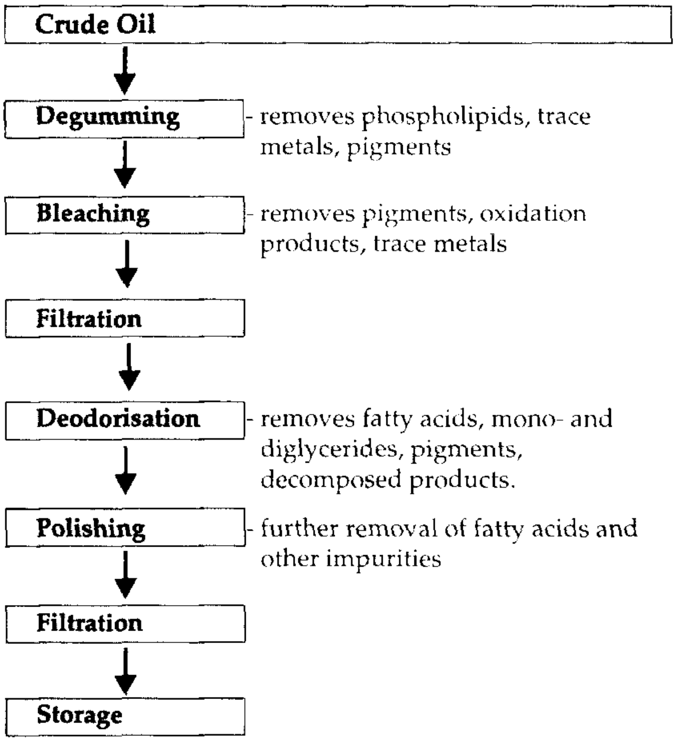
Source: Young (1982)

After refining, all the undesired impurities are removed and an odourless, bland, light yellow oil is obtained. The oil is expected to possess good oxidative and colour stability before it is consumed. However, during storage and before it reaches the consumers, the colour of the refined oil occasionally becomes darker.

Even during deodorisation, instead of becoming lighter, the colour of the oil can become darker. The colour reversion during or after processing could be due to several factors among which are the quality of the crude oils and the manner in which the oils were refined.

The common refining route practised by Malaysian refiners is physical refining. Almost 90% of crude palm oil in Malaysia is refined through this route. *Figure 1* shows the flow chart for the physical refining of palm oil.

Figure 1. Physical Refining of Palm Oil.



Colour Reversion of Palm Oil

Every step in palm oil refining is important and great care is taken in order to produce a stable RBD palm oil with minimal chance of colour reversion. Though in most cases, colour reversion is rectifiable the process adds extra cost.

All aspects of processing have to be handled carefully failing which various technical problems may occur either during subsequent steps in the refining or during storage. Colour reversion during processing is normally associated with poor quality of the crude oils or improper degumming and bleaching processes or faults in the plants and processing conditions. The root cause for almost all colour reversion cases is detectable and remedial actions also can be proposed for most cases. Studies made in the 80s and 90s have suggested that the reversion could be due to coloured pigments present in the crude oil or as a result of the oxidation of alpha-carotene during deodorisation.

a) Low Crude Oil Quality

High quality crude oil is essential for the production of RBD palm oil of low and stable colour. Crude oils contain pigments, carotenoids and other compounds. It was reported that oils derived from badly damaged seeds, and in the case of palm oil, damaged palm fruits, contain brown pigments from decomposed protein and carbohydrates that are resistant to bleaching by adsorption (Swern, 1982). In such cases it is difficult to bring the colour down to its lowest possible level. Furthermore, oxidised crude oils may contain coloured compounds of a quinoid nature developed from oxidation of colouring materials. These oils could be difficult to bleach since new pigments are developed as the old ones are adsorbed. It was also reported that oxidation not only develops new pigments but also stabilises the pigments against their removal by adsorption. In other words, oxidation leads to poor bleachability of the crude palm oil and poor quality of the refined palm oil.

Crude palm oil of normal quality should conform to the specifications as in *Table 2*.

Low quality palm oil is normally associated with a high content of impurities especially the pro-oxidants *i.e.* iron and copper. Both pro-oxidants were shown to decrease the oxidative stability of crude palm oil (Gapor, 1982) and bleachability of the oils (Ames *et al*., 1960). In the crude oil, most of the particulate iron are removed either through the magnetic trap or during the purifier stage in the milling process (Ooi *et al*., 1987) leaving the soluble iron which can be removed at the degumming stage.

Table 2. Guidelines for Crude Palm Oil Quality

Moisture	**0.2% max**
Dirt	**0.05% max**
FFA	**5.0% max**
IV	**50-55**
PV	**10 max**
Iron	**5 ppm max**
Copper	**0.4 ppm max**
Carotenes	**500 ppm min**
Soap	**0.005% max**
Lead	**0.1 ppm max**
Arsenic	**0.1 ppm max**

Source : *Codex Alimentarius, 1992.*
Buyers' Specifications for Crude Palm Oil.

The Deterioration of Bleachability Index (DOBI) is a good measure for crude palm oil quality (Siew *et al*., 1989; Lal & Gasper, 1991). DOBI is basically the ratio between the content of carotene and secondary oxidation products. Studies showed that as the DOBI value of crude palm oil increases, the Rancimat stability of refined oil increases. The relationship between crude palm oil and its bleachability is shown in *Table 3*.

Poor quality crude palm oil due to excessive oxidation can be treated by using more active bleaching earth at a larger dosage of 3.0% and at a higher temperature of 110°C. For high-iron content oil, 0.02% of citric acid of 15% concentration can be added prior to entry to the distillation plant. If the result is not satisfactory, the oil has to be re-bleached and re-deodorised. The amount and type of bleaching earth to be used, depend on the quality of the oil. A lower deodorisation temperature can be used, *e.g.*, at 240°C to remove the remaining colour (Young, 1982).

b) Storage and Handling

Storage and handling are important initial steps for maintaining and producing high quality palm oil. In the handling and processing of palm oil, emphasis is given to avoid and reduce oxidation as far as possible since oxidation is the major contributor towards oil deterioration and has a significant effect on the colour of oils and fats. Oxidation bleaches carotenoid pigments but at the same time develops the colour of other pigments. Partial oxidation causes an increase in the red-yellow colour of vegetable oils due to the formation of coloured compounds of quinoid type (Swern, 1982).

It is absolutely important that all measures are taken so that during handling and storage, oxidation process is kept suppressed and all means contributing towards oxidation are avoided. This can be achieved by using materials that are inert to palm oil such as coated tanks or stainless steel tanks to avoid contamination by iron and other metals and dedicated pipelines to avoid cross-contamination *etc*. Iron and copper are strong oxidation catalysts. Phosphorus is also a pro-oxidant naturally present in crude palm oil. The presence of these substances during deodorisation may lead to colour reversion.

c) Degumming

Degumming is carried out to remove phospholipid gums, trace metals and pigments which are later adsorbed by bleaching clay in the subsequent process. About 0.05% of food grade

Table 3. Relationship between CPO and Bleachability

DOBI Value	Remarks
below 2.0	difficult to refine
2.0 to 2.3	unpredictable
above 2.3	more easily refined

Source : Siew et al. (1989)

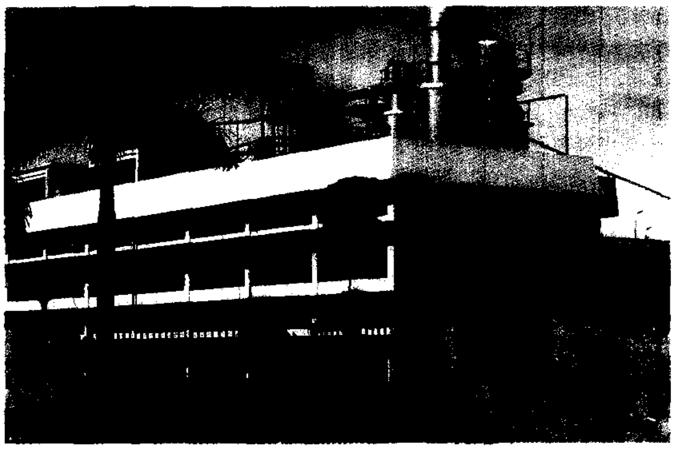
phosphoric acid of 85% concentration is used for degumming at 90°C to 110°C for a short period. Sometimes citric acid is also used but due to economic reasons, phosphoric acid is usually used by Malaysian refiners.

The amount of acid introduced to the oil is quite critical because under dosage or over dosage may lead to a darkening of the oil during deodorisation. Under dosage of phosphoric acid may leave phospholipid lipid gums unhydrated. Phospholipids breakdown at the deodorising temperature leading to a darkening in colour and an impaired flavour stability (Patterson, 1992) while unremoved phosphoric acid also causes the darkening of RBD palm oil (Thiagarajan and Tang,1991). Ong (1981) emphasised that the phosphorus content of crude degummed palm oil should not exceed 20 ppm while Young (1982) stressed that the phosphorus level should not exceed 4 ppm and that of iron and copper should be 0.15 ppm max and 0.06 ppm max respectively. Thiagarajan and Tang (1991) observed that the level of phosphorus in RBD oil affects the rise in FFA and colour development during storage. Gian and Chua (1987) also studied the effect of phosphoric acid dosage on the quality of RBD palm stearin and found that the phosphorus affects the RBD oil.

Increasing phosphoric acid dosage improved the colour but once the optimum colour has been attained, further addition of phosphoric acid increased the phosphorus content in RBD palm stearin. It has been shown that oils with a phosphorus level of less than 4 ppm were more stable than oils with higher levels of phosphorus during shipping (Thiagarajan and Tang, 1991). Howes *et al.* (1991) demonstrated that the addition of phosphoric acid reaches an optimum level beyond which it becomes detrimental to palm oil quality and reduces the performance of the bleaching earth.

The reduction in phosphorus content also brings down the levels of iron and copper because the metals present form complexes surrounded by proteins and phospholipids (Gapor and Ong, 1982). Thus, simultaneous removal of metal complexes is achieved through the precipitation of phospholipids.

For palm oil, the phosphoric acid added disrupts non-hydratable phosphatides by decomposing the magnesium and calcium compounds. It coagulates the phosphatides, attacks and sequestrates the trace metals, *i.e.* iron and copper. Together, they are removed by adsorption on the bleaching earth.


Palm Oil Refinery Plant

Strong phosphoric acid can lead to the phosphorylation of triglycerides resulting in the darkening of the oil during deodorisation. Strong acid also impairs iron removal. Acid is corrosive and can cause corrosion of the mild steel or stainless steel tanks used and introduces free iron in the oil. Rakmi *et al.* (1984) observed an increase in iron content in the degumming process in tanks made of either mild steel or stainless steel. It is therefore important to ensure all metals in contact with the oil must be inert to the oil and free from rust.

The practice of adding calcium carbonate to remove the remaining phosphoric acid prior to bleaching is no longer recommended (Maclellan, 1983; Patterson, 1992) because there is no advantage in adding it before or after bleaching. If it is done, it should be stoichiometrically equivalent to avoid formation of calcium phosphatide which is difficult to remove due to its non-hydratable manner. However, addition of calcium carbonate helps in the formation of phospholipid-metal complex (Chooi and Koh, 1981) hence facilitates the removal of metals as well. The carbonate also attacks the phosphoric acid and protect bleaching earth from reaction with phosphoric acid and thus, retains its performance.

Excessive phosphoric acid reduces the performance of bleaching earth causing the earth to become gelatinous and difficult to separate from the oil at filtration. For this reason, calcium carbonate is used as a filtration aid (Howes *et al.*, 1991). To avoid the risk of calcium phosphatide formation, only sufficient amount of phosphoric acid is recommended (Patterson, 1992). According to Thiagarajan and Tang (1991), increased addition of phosphoric acid would result in PV and FFA instability during storage though it helps in reducing the PV content of the bleached oil. The addition of phosphoric acid can be monitored by analysing the phosphorus content before degumming. As the content of phosphatide in the oil is already known at around 500 ppm, it is seldom analysed unless for a specific reason.

A surplus in acid can be effectively removed by adsorption on bleaching earth. The addition of water immediately prior to bleaching helps to remove the residual iron content and reduces the colour of the bleached oil (Soon *et al.*, 1987). Iron removal by water addition certainly has longer term benefit to the quality of the oil. Gian and Chua (1987) demonstrated that excess acid can be removed by subsequent washing, centrifugation and vacuum drying. However, the degummed oils need to be acid conditioned prior to bleaching for an efficient removal of residual iron. Otherwise poor colour stability will result due to the high residual iron content.

High quality phosphoric acid and calcium carbonate are recommended to be used because the impurities of low quality materials may introduce traces of metals into the oil.

Super degumming method is sometimes used to treat poor quality oil.

ii) Bleaching

Bleaching is done after the degumming process. Literally, bleaching means removal of colour compounds from the oil but in the case of palm oil, removal of colour compounds is not critical at this stage because maximum colour removal is done during deodorisation where carotenoids are thermally decomposed. However, a significant colour reduction in palm oil is observed after bleaching. During the bleaching process, precipitated gums, trace metals, pigments and oxidised products are adsorbed by the bleaching earth and later, spent earths are separated by filtration.

After bleaching, the oil should be free from iron, copper, and phosphorus since all these metals are detrimental to deodorisation.

In Malaysia, bleaching is carried out under vacuum (~50 torr) at 100°C (ranging from 85°C to 120°C) for about 30 minutes. The quality of crude oil, equipment design and processing conditions determine the type and dosage of bleaching earth used. Acid-activated bleaching earth is the type commonly used in Malaysia.

The type of bleaching earth exerts an influence on the final quality of the deodorised oil. Brooks (1989) reported that the non acid-activated bleaching earth is better than acid-activated bleaching earth in terms of colour stability, oxidative stability, FFA content and PV while Howes *et al.* (1991) observed that oil refined with acid-activated earth has better FFA and PV stability than oil refined on non acid-activated earth. Soon *et al.* (1987) reported that refined oil bleached with low quality clay, exhibited less stability in colour, FFA and PV.

Table 4. Bleached Oil Quality

FFA	**<0.15%**
PV	**Nil**
AV	**About half the totox value crude oil**
Iron	**<0.15 ppm**
Copper	**<0.06 ppm**
Phosphorus	**<4 ppm**
Soap	**Nil**

Source : Young, 1982

The particle size of bleaching earth strongly affects the final oil quality and stability. Soon *et al.* (1987) reported that particles of less than 5 microns in diameter are very active as an adsorbent species.

Colour is reduced as the bleaching temperature increases but the rate of colour reversion is faster for oil bleached at higher temperatures. Thiagarajan and Tang (1991) showed that colour reversion in the oil bleached at 150°C is faster than the oil bleached at 95°C. The PV was also poor during storage because secondary and transition oxidation products are not effectively adsorbed at higher temperatures as evident by the increased AV at 110°C bleaching temperature. Total oxidation is minimised at 100°C.

High temperatures are detrimental to oil quality because in the acidic environment (acid-activated bleaching earth needs acidic environment for its activity), formation of FFA and isomerisation of triglycerides can possibly happen. It was reported that temperature is the major process variable that affects the rise in FFA during bleaching.

Howes *et al.* (1991) demonstrated that FFA is minimised when bleaching is carried out at 110°C. They suggested that the optimum bleaching temperature is at 100°C. Adsorption of impurities are highly dependant on the dosage of bleaching earth. The removal of iron, copper and phosphorus is proportional to the dose of bleaching earth (Soon *et al.*, 1987). A sufficient dosage of bleaching earth is needed to adsorb the corresponding amount of impurities. At this stage, though colour removal is not very important, it remains a very useful parameter for measuring the performance of bleaching.

The colour of bleached oil is reduced as the dosage of bleaching earth is increased. But when the dosage reaches a certain level, no further reduction in colour of RBD oils is observed. PV and AV are increased when the dosage of bleaching earth is increased. Since the tests for PV and AV are simple, they are also used as performance parameters for bleaching.

It is important to apply an optimum dosage of bleaching earth to ensure better filtration, less oil loss in spent earth and most importantly reducing the risk of contamination of residual bleaching earth in oil at the time of deodorisation. It was reported elsewhere that the presence of residual bleaching earth at 100 ppm during steam refining can cause colour reversion. This is confirmed by Howes *et al.* (1991) and Soon *et al.* (1987) who found that as little as 0.025% and 0.02% of fines respectively present in the deodorised oil increased the colour and other quality parameters of refined oil significantly during storage. Soon *et al.* (1987) also reported that high levels of fine particles (more than 5 microns) are more likely to pass through filters between bleaching and deodorisation, reducing oil filtration rate and increasing oil retention in the filter cake. In short, the impurities remaining from the bleaching stage in the deodorised oil have no immediate effect on oil quality but will accelerate the increase in colour and other parameters on storage.

In order to reduce the dosage of bleaching earth, one must also be aware that under dosage is detrimental to oil quality particularly the colour of the oil. Under-dosage leads to the presence of residual amount of iron and phosphorus which cause the colour reversion during deodorisation.

The optimum dosage of bleaching earth depends on the quantity and nature of the impurities in the crude oil. It also varies according to the activity of the earth. About 1% of bleaching earth is normally applied in most refineries in Malaysia. A few refineries apply lower dosages of bleaching earth.

The residence time for bleaching is also important as over-bleaching causes the rise in FFA and PV. Colour is also reduced proportionately according to the residence time but maximum colour reduction is not the purpose of palm oil bleaching.

Water addition prior to bleaching was shown to be beneficial in removing impurities from the oil. Addition of water to palm oil improves copper and iron removal, reduces phosphorus content and thus, improves the oxidative stability of the refined oil (Howes *et al.*, 1991).

Sometimes, due to the poor quality of crude oil, some coloured pigments present in the bleaching earth become difficult to eliminate. The coloured pigments may come from the darkening of colourless precursor, destruction of pigments and also modification of pigments. The blue-green colour observed in partially bleached palm oil was studied by Liew *et al.* (1994). They concluded that the colour was formed during bleaching with acid-activated bleaching clays. They postulated that the colour actions were derived from protonation of beta and alpha-carotenes followed by isomerisation and oxidation to form shorter conjugations which were further protonated to form blue-green compounds. The colour disappears after deodorisation.
Siew *et al.* (1994) revealed that the use of silica (Trisyl) in combination with bleaching earth can produce better RBD palm oil. The addition of as little as 0.06% of Trisyl to the bleaching earth improved the colour of the refined palm oil. Better colour stability was also obtained particularly because the phosphorus level in the refined oil was reduced significantly compared to the one without Trisyl. In addition, Trisyl also helped to reduce filtration time, thus leading to a higher throughput in refining.

Combination of activated carbon with bleaching earth was proven to be effective in reducing colour and increasing its stability. Gian and Chua (1987) demonstrated that the addition of 0.1% of activated carbon to 2.0% of activated earth improves the colour of RBD stearin compared to using 2.0% activated earth alone. The colour can be improved further when the activated carbon was dried prior to use. Addition of activated carbon also helps in removing iron.

e) Deodorisation

Deodorisation aims at reducing the FFA, mono- and diglycerides, oxidation products and colour to lowest possible levels. Deodorisation is normally carried out under vacuum (5 torr) at a high temperature, *e.g.* 160°C with live steam injected into the oil. The amount of the stripping steam is about 1% of the weight of the oil. Deodorisation design plays an important role in reducing the undesirable substances. The efficiency and effectiveness of deodorisation depends largely on the design of the deodorisation plant. With the present technology of thin layer pack-column deodoriser, good colour and a low FFA can be achieved at a shorter time, *e.g.* 30 minutes.

Table 5 shows the specifications of the deodorised palm oil.

Table 5. Specifications for Deodorised Palm Oil

% FFA	**0.05 maximum**
PV	**Nil**
AV	**less than 8**
Iron	**0.12 ppm maximum**
Copper	**0.05 ppm maximum**
Phosphorus	**4 ppm maximum**
A.O.M. Stability	**50 hours minimum**

Source : Young, 1982

The carotenoid pigments which give colour to the oil are thermally destroyed at high temperatures. The decomposed pigments, FFA, odoriferous compounds and oxidised products are removed by the action of steam. The rate of removal increases as the temperature and amount of stripping steam increase.

Over-deodorised oil is not stable. Deodorising temperatures higher than say 270°C for a prolonged period cause over-deodorised oil. This oil has lesser amounts of tocopherols and tocotrienols and may contain polymerised, isomerised and randomised products. Maza *et al.* (1992) demonstrated that increasing temperature and steam stripping reduced the stability of fully refined oil. Thermal polymerisation gives rise to polymers and dimers. Howes *et al.* (1993) showed that at temperatures above 260°C, thermal dimers and oligomers can form. The SOS:SSO ratio also decreases as deodorisation temperature increases. Oils refined at a higher deodorising temperature also exhibit poor oxidative stability (Howes *et al.*, 1993). As a guideline, it has been suggested that the upper limit for deodorisation is 240°C for 120 minutes or 270°C for 30 minutes.

f) Other Factors

Ooi *et al.* (1995) investigated the compounds responsible for the perpetual problem of rapid colour darkening of RBD palm oil compared to other edible oils and found that the colour darkening could be derived from beta-carotene.

In the investigation, the sample of palm oil was saponified. It was found that the unsaponifiable matter obtained was yellowish in colour. The yellowish components of palm oil were extracted by column chromatography and further separated by thin layer chromatography technique. Two yellow bands were observed under UV light. Identification of the yellow compounds were then conducted by IR and UV techniques. The authors concluded that the colour compounds consisted of polar and less polar components. The polar component is tentatively identified as hydroxy-alpha-carotene 5,8 epoxide (about 0.4 - 0.7 ppm in RBD palm oil). The other possible carotenoid could be chrysanthemaxanthin whose molecular structure is close to the former. The compounds were believed to be formed from beta-carotene during the degumming step in the refining process. The authors postulated that the formation of the compounds was due to oxidation of unsaturated fatty acids to form alkyl peroxide radicals which then attacked the hydroxy-alpha-carotene to form hydroxy-alpha-carotene 5,8 epoxide. In an earlier study, Tan *et al.* (1985) found that the above compounds found in crude oils were related to para-hydroxybenzoic acid and para-disubstituted aromatic compounds containing NH2 groups.

Conclusion

Colour reversion or darkening of colour during the storage of palm oil, is affected by many factors of which most are controllable. A well-controlled refining process ensures a high quality of the refined product.

It can be concluded from the discussion that:-

i. The quality of crude palm oil determines the quality of refined oil. High quality refined palm oil can be produced from high quality crude palm oil. The quality of crude oil is indicative of its bleachability and the stability of refined oil. It has been demonstrated that DOBI is a good measure for the quality of the crude palm oil. DOBI values of 2.3 and above indicate good crude oil quality.

ii. Colour stability is also influenced by the degumming conditions. Degumming process facilitates the removal of iron, phosphatides, copper and partially oxidised products. However, high levels of phosphoric acid may result in 'slip through' at the deodorisation stage which damages the quality of the oil. Adequate degumming helps the bleaching and deodorisation of palm oil and produces better colour stability.

iii. Bleaching is perhaps the most important step in the refining of palm oil. The quality and stability of RBD palm oil are affected by the temperature and duration of bleaching, type of bleaching earth used, size of particles, dosage, addition of water and presence of fines in the deodorised oil. Sufficient bleaching earth must be added to remove impurities from palm oil. Optimum bleaching of palm oil can be achieved with about 1% water addition prior to bleaching. The bleaching temperature should be around 100°C for 30 minutes under vacuum. Fine particles should also be removed totally by filtration. Addition of Trisyl or activated carbon is also proven to increase the stability of RBD palm oil.

iv. Deodorisation reduces colour, FFA and PV. However the stability of the oil depends more on the manner in which the oil was bleached though deodorisation does contribute to the oil's stability. It is recommended that deodorisation should be conducted at below 265°C to optimise the stability of the refined oil. Higher deodorisation temperatures are able to reduce colour and FFA significantly but lead to reduction in natural antioxidants - tocopherols and tocotrienols and subsequently instability of the oil during storage.

Red Palm Oil

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CHOLESTEROL OXIDES AND THEIR HEALTH IMPLICATIONS

by
Dr. N. Chandrasekharan

The cholesterol-coronary heart disease hypothesis has been of much concern to doctors for a long time. However, the role of cholesterol oxides is not well known. With the advances in methodologies for the detection of cholesterol oxidation products (COPs) by gas and high pressure liquid chromatography as well as the need to further understand the role of lipids in heart disease and cancer, there has been a renewal of interest in the COPs. COPs are formed by the oxidation of cholesterol which is prone to oxidation because of the presence of double bonds.

Some of the more important oxidation products of cholesterol include: 25 hydroxy cholesterol, cholestanetriol and the epoxides. Many food products are reported to contain COPs. Eggs and egg-containing products have been studied extensively, essentially due to their high cholesterol content. Other foods products investigated include milk and milk products and seafood. The concentrations of COPs range from trace amounts to 200 ppm as in unprocessed foods like eggs and during processing can frequently reach 1% to 10% of the total cholesterol content.

The rate and extent of lipid oxidation are dependent on several factors. Conditions that affect cholesterol oxidation include exposure to heat, prolonged cooking time, prolonged storage, packaging, and ionising radiations. Another important element is the level of polyunsaturated fatty acids present, as the development of rancidity depends on the degree of unsaturation. It has been found that meat from animals fed soya oil are more susceptible to lipid oxidation than those fed a tallow diet. Lipid oxidation is catalysed by haemoglobin and the non heme iron.

The formation of oxygen radical or free radical is expected to facilitate cholesterol oxidation. Peroxidation of unsaturated fatty acids precedes cholesterol oxidation. The hydroxyperoxides of polyunsaturated fatty acids formed during lipid oxidation initiate cholesterol oxidation. Cholesterol is readily decomposed when heated with polyunsaturated oils (PUFA), reflecting its instability in the presence of unsaturated fatty acids at high temperatures. It is presumed that free radicals produced from PUFA act as accelerators of cholesterol oxidation, because cholesterol itself is oxidised in a radical chain oxidation system. No COPs are formed when cholesterol is heated alone. However, when heated with unsaturated fats, cholesterol is unstable. The possible association between cholesterol oxides and cancer as well as atherosclerosis has been the subject of much concern. Free radical attack on exogenous cholesterol results in the accumulation of oxides in the tissues. There is now much evidence to demonstrate that several cholesterol oxides are cytotoxic, atherogenic or mutagenic. Various hydroxylated cholesterol derivatives are potent inhibitors of HMG CoA reductase in the aortic cells. Inhibition of cholesterol biosynthesis by these compounds may cause cell death, because of membrane dysfunction. These dead cells could be the primary entry site for lipid infiltration which ultimately leads to atherosclerosis. Oxidised cholesterol, principally the LDL-C is implicated in the etiology of atherosclerosis. Both LDL-C and oxidised LDL are engulfed by foam cells which have receptors for the modified LDL. Atherosclerosis progresses through stages of fatty streak, fibrous plaque and complicated lesion. Atherosclerosis is undoubtedly a disorder of multiple etiology. Many risk factors are involved in addition to hypertipoproteinemia. If endothelial cell modifications of LDL-C is involved in the the atherogenic process, it might be possible to slow it by appropriate use of anti-oxidants, since this modification depends on oxidative damage to the LDL-C molecule.

The presence of COPs in foods raises the question about the safety of consumption of such products. Cholesterol oxidation can be controlled by vitamin E, *i.e.* alpha-tocopherol. Dietary vitamin E supplementation improves the oxidative stability of muscle from fish and this forms the basis of incorporating anti-oxidants into animal feeds. Low temperature or minimum temperature processing is not conducive to COPs formation.

Palm oil with its balanced composition of fatty acids consisting of the saturated, monounsaturated and polyunsaturated is not as vulnerable to peroxidation as the highly polyunsaturated oils. Further, its high concentration of the natural anti-oxidant vitamin E, (tocopherols and tocotrienols) confers protection against free radical formation and so the likelihood of COPs being formed during processing of cholesterol-containing foods in palm oil is minimised. All these positive qualities should reassure consumers of the versatility and nutritional excellence of palm oil.

RESEARCH HIGHLIGHTS

ATHEROSCLEROSIS COULD BE DUE TO BACTERIA AFTER ALL

The idea that bacteria could be the cause of atherosclerosis leading to coronory heart disease, the most common form of heart disease, would have seemed laughable a short time ago but following the recent discovery that most stomach ulcers are due to the bacterium *Helicobacteria pylori*, lends it much greater credibility.

The current issue of the British journal *Science & Industry*, carries a report that USA researchers led by Joseph Muhlestein of the University of Utah Medical School, found high levels of infection by the bacteria species *Chlamydia pneumoniae* in the arteries of people who were being treated for atherosclerosis (hardening of the arteries) where fatty deposits had accumulated on the artery walls.

Out of 90 patients with atherosclerosis, 79% were found to be infected by the bacteria while out of 24 patients without atherosclerosis, only 4.2% had the infection. Of course it could be explained that the bacteria were attracted to the arteries after they were damaged, but the study also showed that very low levels of *Chlamydia* were found in patients whose arteries were damaged by other forms of heart disease. Supporters of the *Chlamydia* theory point out that *Chlamydia* are known to cause chronic inflammation when brought in contact with other tissues of the human body and so they could worsen or even initiate atherosclerosis in the arteries.

As for the 21% of the patients in the study who suffered from atherosclerosis, and in whom the offending bacteria were not found, Muhlesetin's team suggests that this could be either because the immune system had killed them or simply that they were missed due to the very small samples of tissues tested.

The researchers acknowledge that their study is not conclusive proof that the *Chlamydia* bacteria are responsible for the disease and plan further studies. There are too many gaps, inconsistencies, exceptions and contradictions in the present cholesterol-saturated fat hypothesis for the cause of atherosclerosis and this novel *Chlamydia* theory has certainly provided researchers with a refreshing new outlook to investigate the world's foremost killer disease.

PORIM's EXPERIMENTS ON LOW-*TRANS* MARGARINES

by
M. Rasid M. Jaais, Dr M.S.A. Yusoff and Dr B.A. Elias

Margarine can be classified as a consistent fat. It is an initial substitute for butter. Margarine has now established its own image and is fully accepted as a consumer product in its own right. Today, there has been a considerable diversification of the product. Palm oil and palm oil products are excellent raw materials for the formulation of margarine. Margarine based on 100 per cent palm oil products are now marketed in many countries. However, the level of palm oil is restricted mainly due to some consumer constraints.

Since its invention, margarine has been an ideal food that satisfies the growing demands for tailor-made products by both the nutritionist and the consumer. There are three main types of margarine that are formulated for different purposes:

1. Table margarine - tub and packet
2. Industrial or bakery margarine
3. Pastry margarine

In all cases, various oils and hydrogenated or interesterified oils can be used and blended together to achieve the desired attributes. In the case of table margarine, the consistency at temperatures of use is important. For packet margarine, the relevant temperature is 15-20°C in temperate climate and 25°C in hot climates. Tub margarines are expected to have spreadibility at refrigerated temperature of 5-10°C. Industrial margarines have their own physical properties and have to be evaluated by performance testing such as creaming and baking tests. The performance test for a pastry margarine would involve a baking test.

Margarine fat consists of an intimate mixture of glycerides that are liquid and glycerides that are solid at temperature of use. The solid glycerides are present as small individual crystals that have flocculated into a three-dimensional network. The liquid oil is held in this network so that the products appear to be solid but is soft in consistency. Thus in formulating a margarine fat blend, the proportion of solid is adjusted according to the functions required from the product. The solid content should be defined at different temperatures, typically from 10°C to 40°C to cover the whole range of use.

[illegible]

Palm oil is a highly versatile ingredient in margarine formulations. It can be used as a natural colouring material in margarines. Also, its high glyceride content gives consistency without the need for hydrogenation. It contains a fairly high proportion of high-melting triglycerides combined with a relatively low solid content at 10°C to provide margarine containing palm oil, an extended plastic range with good working properties. Its tendency to crystallise in the beta prime-crystalline form will produce a good texture margarine.

Palm kernel oil too is quite commonly used in margarine formulations. Due to its quick crystallisation properties, it is known to give good creaming properties. Its high content of short chain fatty acids gives a very rapid melt characteristic in the mouth and this gives a cool sensation when it melts in the mouth.

[illegible]

Tub margarine has a fairly low solids content at low temperatures that makes it immediately spreadable when taken of direct from the refrigerator. The fat blends have a fairly flat solid fat content profile indicating that the margarine has a uniform consistency over a wide range of temperatures. The fat blends are completely melted at below 37°C *(Figure 2)* and hence have very good oral melt-down. Palm kernel oil and palm kernel olein have steep solid-fat profile and hence have good melt-down in the mouth.

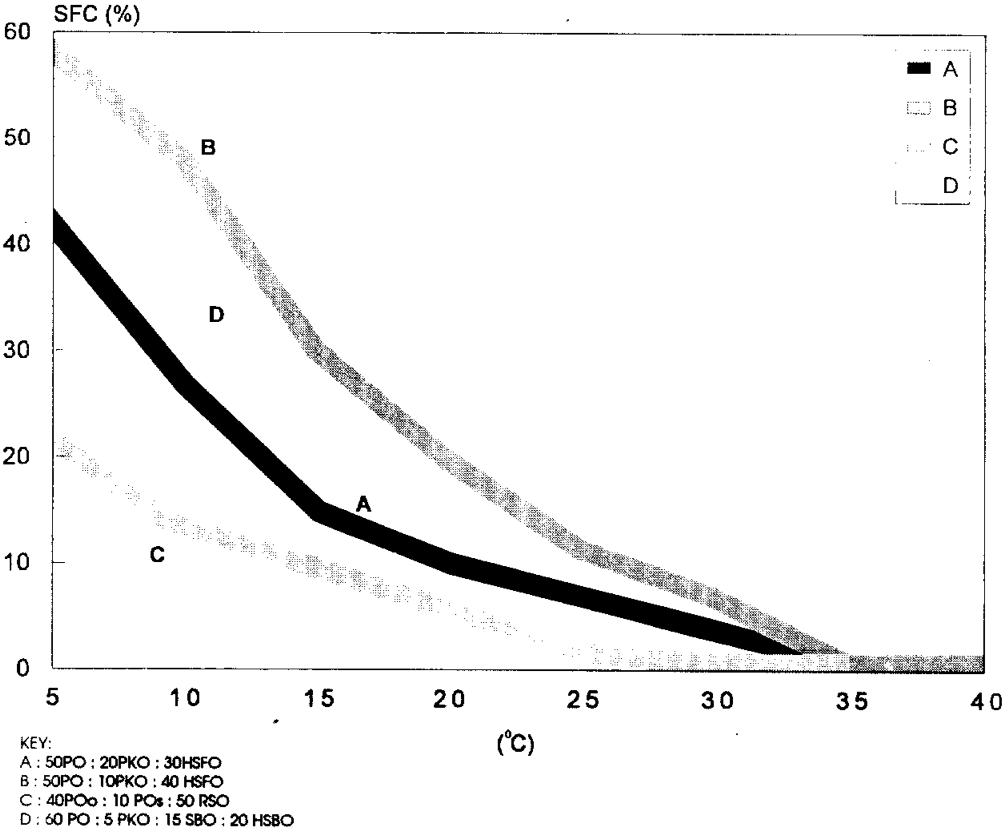
Table 6 shows some table margarine formulations based on palm oil and palm oil products. They have been tested in PORIM and are satisfactory. For standard quality table margarine, up to 40 per cent palm oil can be used in the fat blend whereas for premium quality, about 25 to 30 per cent is the limit. A higher amount of palm olein, up to 60 percent, can be used. Use of palm stearin is rather limited because of its high solid and melting point. Ten percent appears to be the maximum limit applicable. More palm oil (50%) could be used in packet type margarine which resembles butter in consistency in having higher solids at low temperature. Tropical domestic margarine can be produced with 100 percent palm oil and its products.

[illegible] Margarines

Oil/ Formulation	A	B	C	D	E	F
Palm Oil	50	50				30
Palm Olein			40	60	40	45
Palm Stearin			10		7	
Palm Kernel Oil	20	10		5	3	25
Sunflower Oil					50	
HSFO (31°C)	30	40				
Soyabean Oil,				15		
HSBO (36°C)				20		
Rapeseed Oil			50			
TYPE:	Tub	Tub	Tub	Tub	Tub	Tub
SMP(°C):	30.7	33.3	-	-	33.3	-
SFC(%):						Yield Value (S/gm)
5°C	41.7	57.5	20.9	32.0	24.5	2671
10	27.2	47.0	13.3	32.0	-	
15	15.8	31.8	8.3	9.7	-	
20	8.3	20.3	4.0	3.7	8.9	328
25	5.5	11.4	1.6	1.9	-	
30	2.6	7.1	0.5	1.8	-	
37	1.6	1.4	-	-	-	
40	-	-	-	-	-	

**Source: PORIM, 1992*

[illegible] Margarines

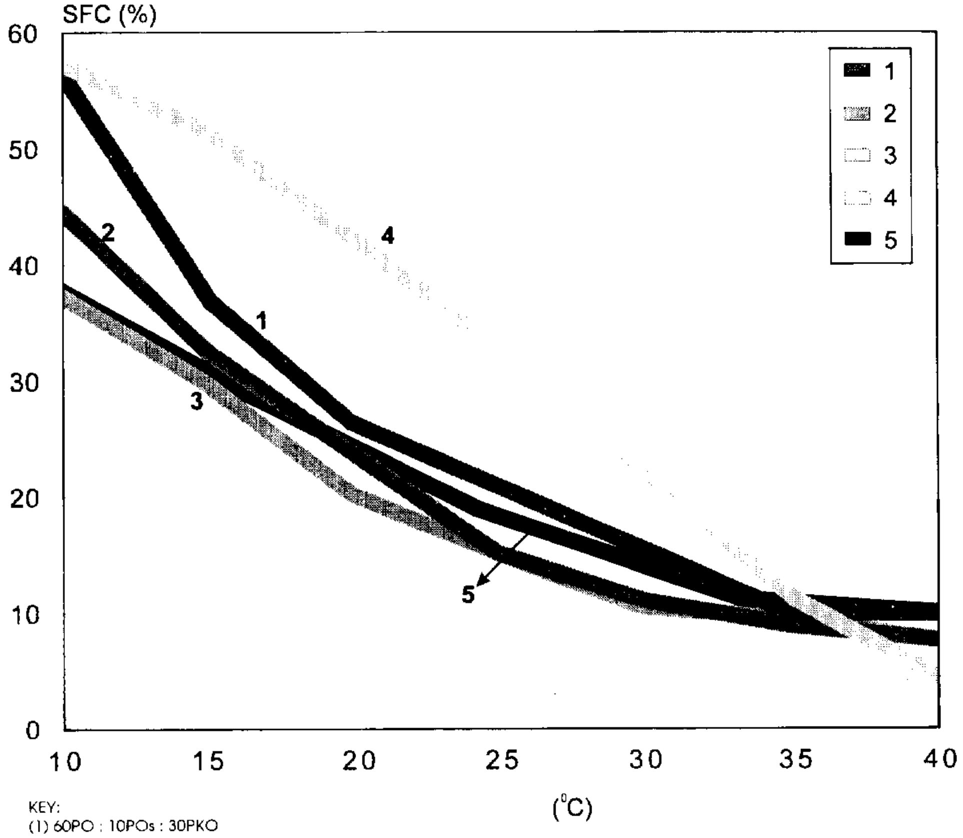


Industrial Margarine

Industrial margarine must be spreadable at usage temperature and must possess a wide plastic range for optimum functionality. This margarine is intended for the production of butter cream, pound cake and short-crust pastry. The properties of this margarine depend to some extent upon the incorporation of air. Industrial margarine has a solid content of about 20 percent at 20°C *(Figure 3)*. Palm oil itself has a solid content close to this, but a blend can improve its functionality. *Table 7* shows some fat blends for industrial margarine. Palm oil and palm stearin could be used in substantial quantity.

It is recognised that oils containing lauric acid such as palm kernel oil have good creaming properties due to their fat crystallisation property. They will promote the formation of small crystall and consequently produce a good homogenous margarine.

Figure 3. Solid Fats Profile of Palm-based Industrial Margarine



KEY:
(1) 60PO : 10POs : 30PKO
(2) 60POo : 30POs : 10SBO
(3) 20POo : 50 POs : 30 SBO
(4) 40 PKO : 50 PO : 10RSO
(5) 60POs : 40RSO

Table 7. Some Formulations of Palm Based Industrial Margarine

Code/Formulation	1	2	3	4	5
Palm Oil	60	-	-	-	-
Palm Olein	-	60	20	-	-
Palm Stearin	10	30	50	-	60
Palm Kernel Oil	30	-	-	40	-
Palm Oil 40°C	-	-	-	50	-
SBO	-	10	30	-	-
Rapeseed Oil	-	-	-	10	40
SFC (%):					
10°C	55.4	44.7	36.5	56.7	36.5
15	38.9	33.2	29.5	47.2	29.9
20	27.9	23.6	20.1	35.7	23.3
25	19.9	14.5	14.8	24.0	17.7
30	13.7	10.8	10.8	15.6	13.7
35	9.1	8.7	8.8	9.8	10.1
40	8.4	6.5	5.7	2.4	7.4

Source: PORIM, 1992.

Low *Trans* Margarine Formulations

The formulations of low *trans* margarines can prepared by either direct blending or interesterification are shown in *Tables 8* and 9.

Table 8 shows the formulations and some characteristics of table margarine. These formulations have been evaluated and are found to be satisfactory. The incorporation of palm oil products can be increased in tub type of table margarine by interesterification process. The interesterification reduces the solid content of the blend to a suitable level *(Figure 4)*. The oral melting properties are correspondingly improved by interesterifying palm oil products with a non-lauric vegetable oil.

Table 9 shows the formulations of palm-based industrial margarine carried out by PORIM. This direct blending of palm products with SFO produces a suitable industrial margarine. This type of margarine requires high solids at 20°C (see *Figure 5*). Thus at this temperature, PO has about 23% solids and therefore is a valuable oil for industrial margarine. Various levels of palm oil products can be used in this type of margarine, ranging from 50 to 100 percent. Palm kernel oil has good creaming properties due to its crystallisation behaviour which enhances its use in almost all types of margarines.

Figure 4 Solid Fat Profile of Low *Trans* Table Margarine

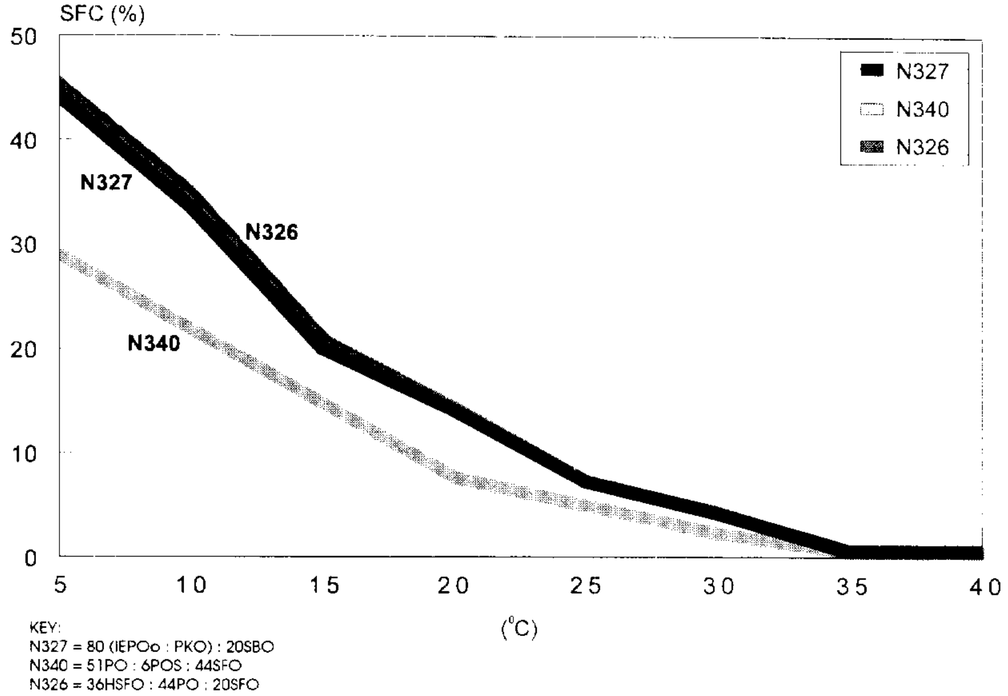


Table 8 Formulations of Low *Trans* Table Margarine

	N327	N340	N326
Formulation	IE(POo:PKO):SBO (75:25) (80:20)	PO:POs: SFO 51:6.5:42.5	HSFO:PO:SFO 36:44:20
SMP°C	31.5	32.2	32.7
SFC(%)			
5°C	43.2	28.2	44.5
10	33.3	20.9	34.9
15	21.0	14.35	22.9
20	14.2	7.20	13.9
25	6.5	4.48	6.4
30	2.5	1.74	2.5
35	Traced	0.48	Traced
37	Traced	-	-
40	-	-	-
Total Trans Content (%)	Less than 1.0%	Less than 1.0%	14.0%

Table 9 Formulations of Palm-based Industrial Margarine

	Code
Formulation	PO:POs:SFO (55:17.5:27.5)
SMP°C	38.6
SFC(°C)	%
5	40.64
10	32.91
15	25.14
20	14.70
25	9.40
30	5.85
35	3.50
37	2.54
40	1.81
Total Trans Content (%):	Less than 1.0%

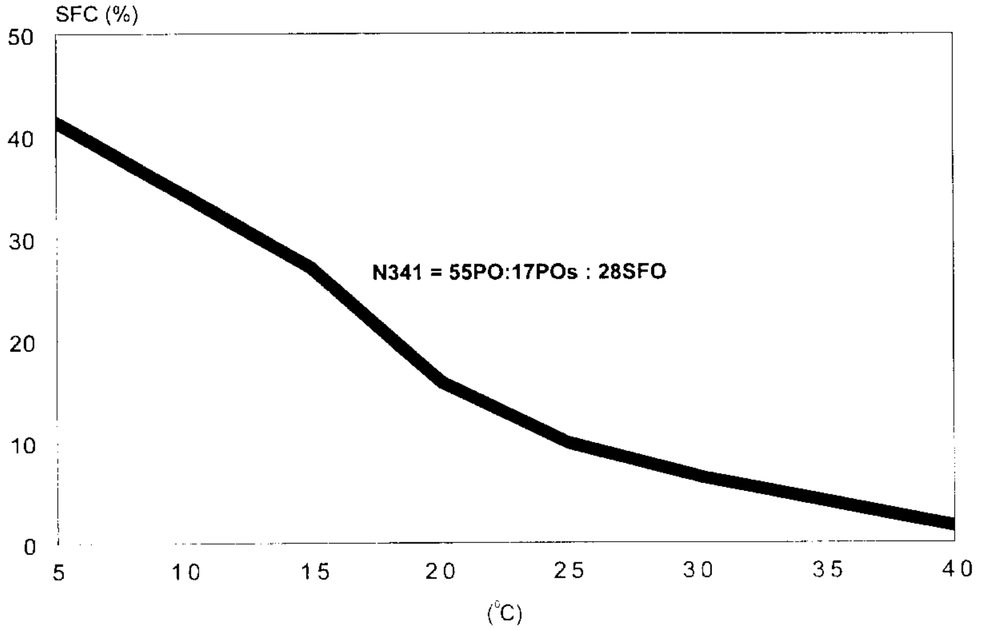
Raw Materials

The raw materials used in the preparation of low-*trans* margarines are SFO, SBO, POs, I.E. POo and I.E.PKO for fat-phase and water, emulsifier, colouring, flavour and salt, for aqueous phase.

Preparation

The preparation for the production of low-*trans* margarine carried out using PORIM's pilot plant, 'Kombinator' that is basically made up of two rotators and a blender. The whole system is cooled by a refrigeration unit attached to it (see *Appendix 1*).

Figure 5 : Solid Fats Profile of Palm Based Industrial Margarine For Russian Market

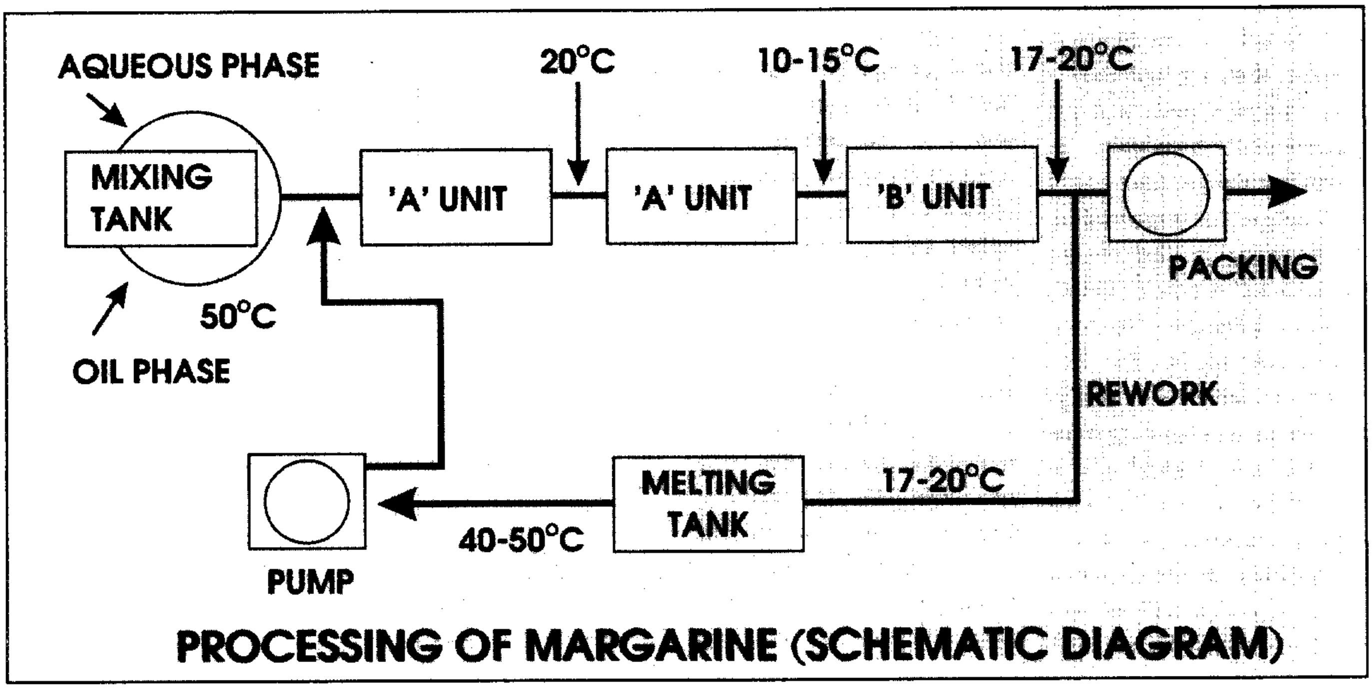


In the preparation of these margarines, the fat phase was heated in the emulsion tank. Then the aqueous phase consisting of water, emulsifier, flavour and colour was slowly added and properly homogenised. The homogenised solution was then pumped into the two rotators. After passing through the two rotators, the products became semi-crystallised. This semi-crystallised solution was then passed through a blender. In the blender, the product was whipped for a few minutes and the finished margarine was filled in containers and stored.

Conclusion

In conclusion, four types of low-*trans* margarines prepared at the pilot plant scale in PORIM were palm-based margarines. Optimum amounts of palm oil and its products were incorporated in blends with either hydrogenated or non-hydrogenated liquid oil namely sunflower oil or soybean oil. The important characteristics of the prepared margarines were analysed and evaluated. By blending with palm oil and its products, the use of hydrogenated oils could be minimised to reduce the total *trans* content in the prepared margarines.

Appendix 1



PROCESSING OF MARGARINE (SCHEMATIC DIAGRAM)

IN BRIEF

Fourth Salon Oil International Trade Fair in Reus, Spain, 28-31 May 1996. (SPAIN - 4TH. SALON INTERNACIONAL OLEICOLA, DEL 28 AL 31 DE MAYO'96)

RED PALM OLEIN HAS ATTRACTED MANY SPANISH BUSINESS VISITORS TO PORIM's BOOTH

by
Mat Rasid Mat Jaais
& B.A. Elias

Small packed bottles of beta-carotene rich oil displayed at PORIM's booth during the Fourth Salon Oil International Trade Fair in Reus, Spain attracted many olive oil business persons visiting the Trade Fair. The red olein created curiosity amongst visitors to the Trade Fair. Some thought that the oil was drinkable like other fruit juices whilst others thought that it was a coloured oil. Those in the oils or fats business assumed that the coloured oil was due to the blending of palm oil with other liquid oils such as sunflower, soya or rapeseed. Whatever it was, the red palm olein appeared to have made deep impression on the many visitors of the Trade Fair.

Officials on duty at the PORIM booth described in detail the actual story of the product. When asked whether such a product was already sold in the Spanish market, they replied that it was still new and not yet commercially available in Spain but the product could be arranged for importation. A company called Pietro Coricelli S.P.A. Olio Di Oliva, expressed keenness to pack red palm olein for the Spanish market. Currently, the company is packing olive oil for its distribution network in Spain and Mediterranean countries. According to a spokesman of the company, it will be very viable to bottle the oil and sell it at price comparable to olive oil if not higher. Moreover, the proposed red oil that he was going to import can be very useful to his business. He can top-up the shortage of olive oil, which at present is very much demanded for household uses. In Spain, olive oil is mainly used in salad dish preparations namely Ensalada Andaluza (Andalusian Salad) and Ensalada De Patatas Con Bacalao (Potato salad with salt Cod). For the main dishes, olive oil is used too. It is used for cooking Pastel de berenjena (Aubergine gratin), Calamares Rellenos (Stuffed Squid), Sepia Estofada (Braised Cuttlefish), Fiambre de bonito (Bonito and olive loaf), Bacalao fresco en papillote (cod en papillote), Tordos con aceitunas (Thrushes with olives), Cabrito con aceitunas y papas arrugadas (Baby goat with olives and wrinkled potatoes), and Ternera con aceitunas verdes (veal with green olives). The company concerned, Olio Di Oliva, estimated the import of about 1,000 tonnes of the red palm oil per year. This beta carotene-rich olein is said to be interchangeable with olive oil for such food dishes to suit the Spanish palate .

In conclusion, PORIM's participation in the Trade Fair was viewed as very successful. Many fruitful technical and business discussions with many business persons were held at the PORIM booth during the event. There was no doubt that by participating in this Trade Fair, PORIM had created a potential market for Malaysian palm oil products in Spain and other Mediterranean countries. Malaysian exporters who are interested, should start to explore business contacts in Spain and enter the Spanish market by supplying palm oil products.

• *FROM PAGE SEVEN*

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We invite readers to send in comments, suggestions and technical news which could be published in this newsletter.

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