later fractionation by solvent.

To conclude, I would like to recall that the crystallization is a dynamic reaction where the molecules of triglycerides are in equilibrium. Many parameters such as the oil composition, the temperature, the polymorphism and the intersolubility may influence this equilibrium. Therefore, depending on the crystallization method used, the quality as well as the yield of the fractions will be affected.

The availability of palm oil fractions has given opportunity for greater adaptability to specific requirements.

The palm oil fractions from single and double stage, blended or not with other oils, followed or not by interesterification, may give new markets. As striking examples we find the superoleins and especially the palm mid-fractions where throughput and cost consideration are of less importance for the high value product.

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Fractionation of Lauric Oils

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ABSTRACT

The different methods of edible oil fractionation are reviewed, and the applicability of these to the fractionation of palm kernel and coconut oils is discussed. Crystallization from solvents such as acetone, hexane or 2-nitro-propane, is the most easily understood account, whence $\frac{1}{2}$ is the convenient for small-scale laboratory trials, but the cost of solvents and the need to flameproof plants makes it uneconomical for an industrial undertaking. Dry crystallization is commonly employed, and there are several methods, described here, for subsequent separation of solid stearin from liquid olein. Chemical and physical properties of the separated stearins and oleins depend on fractionation conditions and on the yields sought. These are reviewed. The properties of the fractions may be further modified by hydrogenation, interesterification, blending or combinations of these techniques.

Many sophisticated confectionery fats are manufactured from lauric stearins and their methods of manufacture and product applications are reviewed. A commercial operation must take care to find a good outlet for the secondary fractionation products (or byproducts) however, and useful outlets for these secondary fractions are therefore considered in addition to those of the main product.

INTRODUCTION

Lauric fats are obtained from various species of palm tree,

TABLE I

Typical Lauric Fat **Compositions**

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the two main varieties being palm, which produces palm kernel oil, and coconut. There are in addition several minor varieties of laurie fat such as babassu, tucum and ouri-curi, but as these are seldom encountered except in the country of origin, and often have specific properties, they will not be considered in this paper. I will therefore concentrate on the fractionation of palm kernel and coconut oils.

Palm kernel and coconut fats differ from nonlaurics in that they contain 47-48% laurie acid, together with smaller amounts of other medium- and short-chain fatty acids. This gives the fats a solid consistency at cool ambient temperatures, but they nevertheless melt below 30 C. Typical fatty acid compositions and melting properties are shown in Tables I and II. The natural fats thus have short melting ranges, which suits them to the manufacture of a variety of fatty foods. Lauric oils have therefore been prized for a wide variety of food stuff applications for very many years. Nevertheless, the fats' melting points and solid contents at room temperature are a little low for production of confectionery coatings and couvertures, a drawback that can be alleviated by fractional crystallization and separation of the harder and softer components.

The advantages of fractionation were first appreciated

TABLE II

Typical Lauric Fat Properties

Fat		Solid fat contents (% by pulse NMR)				Slip	
	LV.	N ₂₀	N ₂₅	N30	N35	N40	$M.$ Pt. ($^{\circ}$ C)
Palm kernel oil	17.5	44	20	0			28
Palm kernel stearins	9	70	48	8	Ω		30
		82	68	29	0		32
		94	84	37		റ	34
Palm kernel stearin $(IV = 7)$ hydrogenated to lower IV		87	70	24			31
	0.4	95	90	50			35
Palm kernel stearin $(IV = 7)$ refractionated to lower IV		94	90	60		Ω	33
Coconut oil	8.5	36	Ω				24
Coconut stearin	4	84	53		0		30
Hydrogenated coconut stearin	1.5	92	57	8			32
Hydrogenated palm kernel olein	1.0	73		27	14	6	41

by European fat companies who imported coconut oil from Sri Lanka in long wooden barrels called "Ceylon Pipes." The pipes were filled with warm fluid oil which cooled slowly during the sea voyage to cooler European climates. This slow cooling, perhaps coupled with the gentle agitation of the ships' movement, allowed the fat to crystallize and separate into fractions. Companies receiving batches of the partly crystallized fat evaluated the properties of the separate components and realized that the harder stearin fraction could be put to good use in the couverture and coatings industry. Nowadays there are various methods for fractionating lauric fats. Nevertheless, they all lead to the production of a secondary fraction, or byproduct, the successful sale of which lies at the heart of profitable business.

It is also possible to modify the properties of the lauric fats by partial or complete hydrogenation, a process which generates no byproduct disposal problem. Many oil and fat refineries therefore offer a range of unhardened, partially hydrogenated or fully saturated fats for use in substitute coatings, biscuit filling creams, coffee whiteners, and many other applications in the food industry. Hydrogenated laurics are cheaper than lauric stearins. While excellent in many respects, hydrogenated lauric fats lack the very high solid contents at 20 and 25 C, and the very rapid melt between 25 and 35 C of the lauric stearins. The bloom resistance of coatings made with hydrogenated palm kernel oil is also inferior to that of palm kernel stearin coatings (1,2). While these deficiencies can to an extent be alleviated by the addition of surface active agents such as sorbitan stearates and polyoxyethylene derivatives, it is sometimes stated that claims for the efficacy of these agents are exaggerated (3). Emulsifiers and surface active agents can in any case be used to further modify the properties and performance of lauric stearins. These latter products therefore stand apart, superior to hydrogenated lauric fats in many food applications. Nevertheless, the benefits of fractionation and hydrogenation can be combined, and it is now customary to subject palm kernel stearins to a mild hydrogenation. The properties of a few typical hydrogenated palm kernel stearins are shown in Tables I and II. Patteson (4) has reviewed aspects of hydrogenating lauric fats and fractions.

FRACTIONATION PROCESSES

Several methods may be used for lauric fat fractionation. Solution of the melted oil in an organic solvent such as acetone, hexane or 2-nitropropane (5), followed by cooling and filtration to remove crystals of the higher melting component, is easily applied in the laboratory, but is expensive industrially due to the costs of solvent recovery and fire prevention measures. Dry crystallization is commonly used, and there are several methods for subsequent separation of solid stearin from liquid olein. High stearin yields are possible and are therefore sought. The cooled, partly crystallized fat "sets up," making continuous operations, e.g., with a rotary drum filter and string discharge, of Florentine filter, inapplicable. The semisolid fat can be subjected to hydraulic pressing, e.g., in canvas bags. Alternatively, a fluid medium may be maintained if the oil is previously diluted with a sufficient quantity of liquid olein from a previous run to reduce the solid content of the partly crystallized mass to about 20%. This mixture may then be separated into hard and soft components by rotary drum filtration, or by the detergent "lipofrac" process. There are also two distillation approaches. In one of these methyl esters, e.g., of lauric myristic and/or palmitic acids are added to the oil together with a low-temperature interesterification catalyst. The low-chain acids are, in random manner, converted to methyl esters which distill out of the mixture, the longer chain acids being incorporated into the triglycerides (6,7,8). In a second procedure the fatty acids are liberated from the glycerides and fractionally distilled to give a fatty acid mixture of desired composition which is then reesterified with glycerol. When this latter approach is used to give hard lauric fat fractions for use in the pharmaceutical industry, an excess of glycerol may be used to generate a fair proportion of diglycerides in the final product (9,10,11). However, the fractional crystallization process is most widely used.

In all fractional crystallizations the size, shape and number of the crystals is important, as these features influence the subsequent separation of the liquid oil. Large crystals with little oil inclusion are required. The crystals should be compact, not needle-shaped.

The crystallization process can be divided into three basic steps of:

• supersaturation of the liquor or supercooling of the melt,

• formation of crystal nuclei, and

• crystal growth.

The first step is important due to the aspects of triglyceride polymorphism and morphology. Vegetable fats can crystallize in several polymorphic forms, the most common being alpha, beta prime and beta (12), which in the same order display an increasing stability, melting point, heat of fusion and density. In general the lauric fats here are stable in the beta-prime form (12). The rate of crystallization of the alpha form is higher than that of the beta-prime, which in turn crystallizes faster than the beta form. A high degree of supercooling induces a rapid solidification of alpha phase crystals, and as a result a large number of small crystals will result, which is undesirable. Even if these alpha phase

crystals subsequently transform into the beta-prime form there will still be a larger number of crystals. Small crystals are formed because at a high degree of supercooling the rate of nucleation is high whereas crystal growth is slow due to the high viscosity of the oil. Fractional crystallization should therefore be carried out at a low degree of supercooling with gentle agitation to overcome the effects of the high *viscosity* and allow release of the latent heat of crystallization. Processing times are accordingly long.

Crystallization from a solvent offers several advantages. Fats generally crystallize from solvent in the stable crystal form, and as the viscosity is reduced heat transfer throughout the medium is improved. Crystal growth is also generally faster than in dry crystallizations enabling shorter process times. *Moreover* there is *less* oil inclusion, and the split between stearin and olein can be more specifically controlled. The main disadvantages are that solvent must be recovered and more cooling must be applied, depending on the nature of the solvent, as there is a large bulk and crystallization takes place at a lower temperature than in the absence of solvent. Above all, however, the precautions necessary to prevent fire are the main drawback. *Solvent* fractionation is therefore an expensive process only applied for the production of high-quality materials. The solvents used may be acetone, hexane or 2-nitropropane (5,13,14,15). The oil is conveniently heated to about 40 C to ensure complete melting, and blended with warm solvent in the ratio of 1 part oil to between 3 and 5 parts solvent (by weight). The solution is then cooled, eg., in a scraped-surface crystallization vessel, the agitation in which is adjusted to compromise between the needs of adequate heat transfer and avoiding attrition of the growing crystals. Crystallization temperatures vary depending on the nature of the solvent, the concentration of oil in the solution, and the characteristics needed in the final fractions. With acetone solvent, for instance, temperatures of between -2 and 20 C have been used to give stearin IV's of between 1.8 and 8.3 units (15). In a batch process the crystals may be allowed to settle, the mother liquor being removed by decantation or syphoning. The crystals should be washed several times with solvent at the crystallization temperature, after which they are recovered and stripped of residual solvent. Alternatively the solid phase may be removed and washed in a continuous filtration unit. Adequate washing to remove mother liquor is an important, but sometimes neglected, part of the process.

In contrast to the expensive solvent fractionation, dry fractionation is much cheaper, and with laurie fats satisfactory products may still be obtained on account of the reasonable rate of crystallization and simple polymorphic behavior, in comparison with other fats.

The oil may be cooled slowly with gentle stirring until it has a plastic consistency. It is then poured into canvas bags and allowed to cool further to the fractionation temperature, at which it is stabilized before being subjected to

TABLE III

hydraulic pressure (16). In some cases the stearin so obtained is refractionated to improve its characteristics. It is possible to automate this procedure by cooling the oil in a scrapedsurface crystallizer until it is semifluid, whereupon it is filled into trays or boxes which pass through a tempering room before being subjected to mechanical pressing as before.

Fluidity may be preserved by prior blending of the melted oil with a sufficient quantity of liquid olein from a previous run. The blend is then cooled and allowed to stabilize, usually for about 6 hrs, at the fractionation temperature. In this case the separation may be by continuous filtration, e.g., on a rotary drum or by Tirtiaux processing. Alternatively the Lipofrac system may be used in which an aqueous detergent solution is added to the slurry to assist the separation of liquid olein and solid stearin (16,17,18,19). The aqueous solution contains about 0.5% of a detergent such as sodium lauryl sulphate, which preferentially wets the surface of the crystals displacing the liquid oil. The aqueous solution also contains about 2% of an electrolyte such as magnesium or aluminum sulphate to assist coalescense of the liquid olein droplets. Separation is then effected by centrifugation. The heavier phase containing the aqueous detergent solution and the suspended solid stearin crystals is then heated to melt the stearin, whereupon it separates out as a lighter liquid oil phase and can be removed in a second centrifuge. Table III shows some typical processing results, while Figure 1 illustrates a flow diagram in which olein is used to dilute the feedstock.

The resulting fractions are refined and deodorized by conventional means. Rek and Appel have described methods for the determination of residual detergent (21).

Table III gives an outline of processing conditions and yields with the detergent fractionation process. These figures are also applicable, in general terms, to other forms of fractionation. It can be seen that the original IV and FFA of the oil influence stearin yield, higher IV's and FFA's, giving a lower stearin yield if the processing conditions are maintained constant. The oil of initial $IV = 17.2$, and $FFA = 8.4%$ thus gives a better yield of lower IV stearin than an oil of IV = 17.7 and FFA = 9.5%. With oils of higher IV and/or FFA, the yield can be restored by use of a lower processing temperature, but in this case a stearin of higher IV, and thus lower quality, is obtained. The requirement for a feedstock with low FFA and low IV can present a dilemma to fractionation plant managers, as Nigerian PK oil usually has a lower IV but higher FFA than does Malaysian oil.

PROPERTIES AND USES OF LAURIC STEARINS

The compositions and properties of laurie stearins are shown in Tables I and II. Fractionation increases the laurie (C_{12}) and myristic (C_{14}) acid concentrations in the resulting stearins and leads to a corresponding fall in the levels of

FIG. 1. LIPOFRAC processing.

short chain (C_6-C_{10}) and unsaturated (C18:1 and C18:2) fatty acids. As triglycerides containing the short-chain and/or unsaturated acids are removed simultaneously by fractionation, iodine value (IV) is a very good parameter for quality assessment, lower IV palm kernel stearins (PKS's) having better physical characteristics. This is shown in Table II, where it can also be seen that an understanding of the processing history is important. Quality is generally assessed in terms of high solid fat contents (SFC's) at 20 C and at 30 C, and a low SFC at 35 C, as these features ensure good "snap," good finger point resistance, and good meltdown, respectively, in substitute chocolate goods made with the stearins, the main area of use. The IV of a PKS can be further reduced by a lower initial fractionation temperature, by refractionation of the stearin initially produced, or by hydrogenation. These three processing techniques lead to slightly different products. When PKS's of very low IV are produced in a single fractionation run, e.g., by solvent fractionation, the concentration of laurie acid falls back toward that of the initial oil, and there is a further increase in the myristic and palmitic acid contents. This is not the case when an initially produced PKS is refractionated to lower IV, as in this case the initially high laurie acid content is maintained, there being a smaller increase in the myristic acid concentration. Hydrogenation does not, of course, change the laurie, myristic or palmitic acid levels, but instead converts the unsaturated C₁₈ acids into stearic (C18:0). These chemical differences are reflected in differences in the physical properties, the hydrogenated PKS's having higher melting points and higher solid fat contents at 35 C. A PKS refractionated to lower IV has a higher N30 value, giving better finger point resistance than a PKS fractionated to an initially low IV.

Hydrogenation of a PKS has several advantages over the other techniques, and is the procedure most often used in industry. In addition to giving a better product yield based on the initial feedstock oil, the resulting fats have improved color and flavor stabilities. Furthermore, the crystal structure of substitute chocolate manufactured with an HPKS is finer than that of one made with unhydrogenated PKS. There may be at times, however, sound commercial reasons for trading unhydrogenated PKS. For instance, import tariff categories may be more lenient. In these cases it is often recommended that a small proportion of fully hydrogenated palm oil should be added to the PKS to act as a crystal seeding agent (21). No such seeding agents are needed with HPKS products.

Coatings made with HPKS's are excellent for short shelf life substitute chocolate goods. They have a rapid melt at mouth temperature, and yet do not melt on the fingers. As the fat is initially stable in the beta-prime form the coating needs no tempering, and provides an excellent satinlike gloss to the product.

Both PKS's and HPKS's have glycerides which are both chemically and physically different from those of cocoa butter. Eutectics therefore develop (23) when they are blended with cocoa butter, i.e., the fats are incompatible. Palm kernel stearins are called "cocoa butter substitutes" (CBS's), and are used as total replacements for cocoa butter in special recipes, as shown in Table IV. Lauric fats gradually transform from the initially stable beta-prime polymorphic form into beta crystals. This slowly leads to fat bloom, such as that shown in Figure 2. The thumb and finger print impressions on either side of the HPKS bar can be clearly seen, while the delayed bloom due to prolonged storage is just visible on the surface of the bar. There is no bloom on the

TABLE IV

Typical **Recipes for** Chocolate and Substitute Oaocolate Coatings

Substance	Conventional milk chocolate	with HPKS with HPKS	Light coating Dark coating
Cocoa mass	12.5		
Cocoa powder (10-12% fat)		6	12
Full cream milk powder	32		
Skim milk powder		16	
Sugar	37	45.6	56
Added fat (CB or PKS)	18	32	31.5
Lecithin, flavors, etc.	0.5	0.4	0.5

FIG. 2. Bar of substitute chocolate **made with** palm kernel stearin. **Advance..d bloom** can be **seen where poor handling left** fingerprint in the contract of delayed bloom, due to long storage, is just starting on surface of bar. **There is no bloom on the broken edge of** the **bar.**

broken edge. Gloss retention is improved by the use of surface active agents such as sorbitan stearates, but retention of more than six months cannot usually be guaranteed. The presence of longer-chain fatty acids, e.g., HPKS's initially of high IV (say 10-12) but hydrogenated down to lower IV, or contributed by other fats such as cocoa butter, speed bloom development (1). Coatings made with PKS's must therefore conform to low cocoa butter, low milk fat formulations, such as those shown in Table IV. A further problem with laurie fats is that they sometimes develop "soapy rancidity." If any lipase or other enzyme is introduced into the coating, e.g., from the milk powder, this may promote hydrolysis of the triglycerides. The liberated laurie acid has a distinct soapy flavor which can be detected even at low levels (24).

Coconut stearin has a much quicker melt than does palm kernel stearin, and even after hydrogenation it is not suitable to use in normal substitute chocolate coatings, the very low solid fat content at 30 C causing considerable melting on the fingers. It does find some application in enrobings for ice cream, where the quicker melt is advantageous at the cooler mouth temperatures prevailing. The main applications of coconut stearin are in biscuit filling creams and chocolate centers, where the rapid melt gives a pleasing cooling sensation on the palate, and leads to a very fast release of fatsoluble flavors, and improved flavor impact.

PROPERTIES AND USES OF LAURIC OLEINS

While fractionation of laurie fats produces useful highquality stearins, the softer olein byproducts do not usually command the same up-market image, and they can become a drag on the market. As shown in Table III, they are usually obtained in greater yield than the stearin, and invariably have higher FFA contents than the parent oil. Any deleterious components, such as diglycerides, also tend to concentrate in the olein only if fractionation conditions are so designed to obtain the highest quality stearins. Nevertheless there are several uses, the simplest of which is to blend the olein back into defatted meal used in animal feeds where a minimum residual fat content commands a price higher than that of fully defatted meal. Alternatively the olein can be added at a low level to stocks of parent oil scheduled as hydrogenated palm kernel olein. These are not too different from those of hydrogenated palm kernel oil itself, but nevertheless offer some advantages in the production of filled milk and coffee whiteners. Coconut olein is rich in shorter-chain (C_6-C_{10}) acids and is a useful feedstock for medium chain triglyceride (MCT) production (25). Other attractive possibilities are in the interesterification of laurie oleins with hard nonlauric fats such as palm stearins. Berger has already studied several possibilities in this area (26), while work directed by the author led to several patented products (27,28). Table V shows some typical products and applications, based on interesterified mixtures of soft laurie oleins and hard palm fats.

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TABLE V

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Hydrogenation of Palm and Lauric Oils

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ABSTRACT

The technology and equipment for hydrogenating fats and oils is described. Advantages and disadvantages of various batch and continuous processes are discussed. Continuous hydrogenation is suggested for plants that process essentially only one type of oil. When several different feedstocks are to be processed in the same equipment, batch autoclaves may be advantageous.

Hydrogenated palm kernel and coconut oils or fractions have many uses in food products, especially in products where specific melting points and good oxidative stabilities are important. Trends in hydrogenation indicate that more and more energy-saving and automation devices will be used to reduce energy and labor costs and to make more uniform products, especially in batch processes.

INTRODUCTION

Among the modification processes of edible oils and fats catalytic hydrogenation is by far the most important. By Wilhelm Normann's invention in 1911 a sufficient world supply of hard and spreadable fats was secured, In 1980-81 liquid oils including fish oils represented almost 57% of the total annual production of oils and fats worldwide (Table 1).

The main reasons for hydrogenating oils are to solidify liquid and semiliquid oils and to improve the oxidative stability. Solidification, of course, includes modification or amelioration of such rheological properties as plasticity, spreadability and hardness of fats which are already solid at ambient temperatures.

Palm and laurie oils belong to this type of fats. Large quantities of these fats are used for human consumption as such without modification. Also, large amounts are subjected to fractionation, hydrogenation and interesterification. Hydrogenation in this ease is only one process among others. Nevertheless, it is indispensable in the concert of procedures at hand for preparation of specialty fats.

Dealing with the hydrogenation of palm and laurie oils today includes the hydrogenation of their derivates obtained by fractionation processes. The oleins and stearins of palm and palm kernel oil are of extraordinary importance. Recently coconut oil fractions, too, acquired increasing interest.

Prior to a short description of the various applications of all the numerous fats available the modern technology of fat hydrogenation shall be discussed.

TABLE I

Total World Production **of Edible** Oils and Fats in **1980-81 a**

asource: *Oil World.*

MODERN TECHNOLOGY OF FAT HYDROGENATION

Hydrogenation of oils and fats is a very complex process, controlled mainly by: starting and hydrogenation temperatures, hydrogen pressure, type and amount and catalyst, design of the hydrogenation reactor and type and quality of the oil. From one input raw material a great number of finished products with widely differing chemical and/or physical properties can be obtained (1-8).

Total hydrogenation with complete saturation of all double bonds $(IV<1)$ is normally of limited interest for edible fats. Exceptions are the laurie fats, which are mainly treated in this way. Other totally hydrogenated fats with extremely high melting points are transferred into edible