

## Types of Pre-treatment

The main types of pre-treatment are :

- (i) *De-gumming* or *de-sliming*. This is usually used with soyabean and other oils with a high content of phosphatides and other unsaponifiables. Warm water, sometimes with about 0.1% of phosphoric acid, is added to hydrate some of the impurities which are then separated in a centrifuge to leave a relatively dry, clean oil. Commercial lecithin is recovered from the other fraction, particularly in the case of soyabean oil. These gums, known generally as 'break' material, can also be separated by heat.
- (ii) *Acid refining*, is carried out with concentrated sulphuric acid in the pre-treatment of linseed, and other drying oils, for use in paints. The strong acid chars the phosphatides and related materials. Treatment with sulphuric acid is also used to clean up low grade materials prior to splitting with water (particularly by the Twitchell process).
- (iii) *Alkali*, or *soda*, *refining* is normally included in the preparation of fats for edible purposes. It is not commonly employed in the pre-treatment of soapmaking fats, but it can be useful to upgrade certain tallows for use in high quality soap bases. An excess of caustic soda (or sometimes sodium carbonate) solution is used to neutralise the FFA in the fat and to carry away in the lower aqueous soapstock layer other impurities, plus some neutral fat. Careful attention is necessary to avoid an undue loss to the soapstock of good neutral fat.
- (iv) *Steam distillation* can be used to reduce the free fatty acid content of a fat; a process which has been employed particularly with fairly high FFA palm oil. The fatty acids separated are used in soap. The relatively high temperatures involved bleach some fats, particularly palm oil; but some colouring matter tends to be 'set', and so more difficult to remove after the treatment.
- (v) *Deodourisation* is a steam distillation process carried out under fairly high vacuum to remove odiferous and taste producing impurities from fats. Deodourisation of edible fats is normally carried out on materials which have been soda refined and bleached; otherwise FFA would be removed in this process with other volatile constituents and this is better done by soda refining. The process is sometimes used to remove highly odorous constituents from coconut and palm kernel oils to be included in high proportions in certain toilet soaps. Metal scavengers, such as citric, tartaric and phosphoric acids are often added to fats prior to deodourisation.

develops; and chemical bleaching is not used with edible fats, or, usually, with fats to be made into the better quality toilet soaps.

The oxidation can be carried out with air (or oxygen), with alkali dichromate (plus acid), with sources of available chlorine, or of chlorine dioxide, or with other reagents. Air can be blown through hot palm oil to produce air bleached palm oil. Soap made from this oil has a slight brownish shade and a characteristic odour. These qualities limit its use, but it has been employed in orange/red carbolic toilet soaps. Bleaching of palm oil with chromic acid is very effective. The oil is agitated with air for several hours after addition of sodium dichromate, salt, and hydrochloric acid. After the mix has settled, the aqueous layer is run to waste and the oil is washed several times with water. More recently, most chemical bleaching processes have used chlorine compounds.

Oils and fats, particularly acid oils, can be bleached under acid conditions. Sodium chlorite is usually employed, activated with acid; and the active species is thought to be chlorine dioxide ( $\text{ClO}_2$ ). The bleaching of tallows and greases by using sodium chlorite plus sufficient sulphuric acid reduces the pH to 4, or below. It has been found that no additional activator is necessary if the fatty matter contains sufficient FFA (usually above about 20%); and when the fat is not sufficiently acidic, the preferred activator is phosphoric acid. About 0.5–1.0% of sodium chlorite is used. The process can be carried out in a simple vessel in which agitation is provided by compressed air from a perforated pipe. The vessel can be constructed of mild steel, but stainless steel is preferred. Alternatively, continuous bleaching plants can be designed for use if the scale of operation is sufficiently large. When phosphoric, or other mineral, acid is used, particular care must be taken to avoid addition of reagents when no fat is present; otherwise an explosion is liable to occur. The bleached fat should be saponified as soon as possible. Soaps made from chemically bleached fats tend to deteriorate more than those made from adsorption bleached materials.

Chlorine compounds can also be used under alkaline conditions to bleach soaps, including soapstocks. Soapstocks should be completely saponified, and soaps should preferably be washed to remove the glycerol before the bleaching operation. Sodium hypochlorite has long been used to bleach soap in the pan, but, particularly for soaps containing some palm material, there are advantages in using :

- (i) Sodium hypochlorite activated with hydrogen peroxide.
- (ii) Sodium chlorite activated with sodium hypochlorite, although various other activators are possible.

contained about 64% TFM and 0.3% NaCl. Wigner deduced his rule as an empirical observation from a study of large numbers of boils, which showed that when a pan contents has been grained and settled,

$$\frac{\text{Percentage salt in soap curd}}{\text{Percentage salt in lye}} = 1 - K_s \frac{\text{Percentage TFM in curd}}{100}$$

$K_s$  is nearly constant for almost all soaps, with a range of about 1.50–1.53, average 1.515. If electrolytes other than salt, particularly caustic soda, are present in significant quantities, equivalent salting out figures must be added to the salt concentrations. By substituting salt in soap curd = 0, it follows that for a salt-free curd, the percentage TFM in curd equals  $100/K_s = 100/1.515 = 66\%$ . Table 5.1 gives some analytical data for full scale boils of different types of soap presented by Wigner in support of his rule.

Wigner also found that the 66% rule could be applied to fitted pans using ‘free solution’ in place of lye. Free solution is defined as water which is not combined in the 66% TFM hydrate. For the neat soap which separates when a fitted pan is allowed to settle, Wigner says that ‘neat soap is a soap hydrate of a composition which varies according to the concentration of salt in the free solution, always containing more water than the hypothetical 66% hydrate, and containing a small amount of salt which increases with the increase in the degree of hydration’. Figures in support are given in Table 5.2. It will be seen that as the concentration of electrolyte in free solution falls and the fit becomes ‘finer’, or ‘closer’.

**Table 5.1.** Data in support of the 66% rule for soap curds.

TFM % in soap	NaCl % in lye	NaCl % in soap		$K_s$ †	TFM % in soap hydrate
		Found	Calculated		
53.7	9.5	1.76	1.76	1.518	66.0
52.3	9.1	1.87	1.89	1.520	65.9
54.6	9.0	1.44	1.56	1.538	65.0
57.8	8.8	1.10	1.10	1.514	66.0
56.0	8.7	1.33	1.32	1.513	66.1
53.5	9.1	1.69	1.71	1.522	65.7
57.1	8.2	1.17	1.10	1.501	66.6
57.8	9.4	1.17	1.17	1.516	66.0
58.0	9.1	1.12	1.10	1.512	66.2
56.7	9.2	1.34	1.30	1.506	66.3
54.7	9.6	1.68	1.65	1.508	66.3

† The column for  $K_s$  has been added by the present author.

Fitting, as carried out in the traditional way, requires skill and experience; and is best learned by personal tuition by an experience soapboiler. The soap mass is boiled extensively; and the end point is judged by the look of the boiling soap and by the way it leaves a heated trowel. The soapboiler's trowel test is carried out using a bricklayer's trowel. The trowel is heated by immersion in the boiling soap, after which the adhering soap is scraped off. The trowel is then again immersed, drawn out edgewise and tilted to about  $60^\circ$  to see how the soap runs off. A soap which is too close for a typical medium/fine fit travels slowly, is apt to stick to the trowel, and the trailing edge tends to leave streaks of soap adhering to the blade. A soap which is too open slides off the trowel fairly rapidly and breaks into a number of small pieces. In the ideal condition the soap film should be transparent; and should slide slowly and steadily from the trowel, leaving the surface of the trowel clean and bright. It should break up into two, or three, large broad flakes. The trailing edge of the moving film should thin out gradually to an almost imperceptible transparent wafer of soap which may extend to  $\frac{1}{4}$  inch behind the main body of soap.

The actual yield of usable neat soap is less than that which might be expected from the loss of nigre, because crusts of solid soap form on the soap surface and on the sides of a pan which has cooled during settling; and so cannot be cleansed with the liquid neat soap.

As mentioned earlier, soap given an open fit settles relatively rapidly, and neat soap suitable for soap powders, and for household soaps made using the modern chilling and extrusion processes, can commonly be cleansed after 1–2 nights settling, instead of the 3–4 nights needed after a medium/fine fit.

### **Wigner System of Quantitative Soapboiling**

The data can be collected from experimental boils for the phase equilibria for the various fat blends used in a factory. If the composition of the pan contents is known, it is then possible to calculate what additions should be made to achieve a desired wash, or fit. A problem in the application of this idea is that steam condenses as the soap is boiled with open steam, so that it is difficult to know how much water is present. Also, the density of the pan contents is influenced by the bubbles of steam and total mass cannot be determined by staffing to measure volume. These difficulties can be overcome by the use of a pneumercator type of gauge shown diagrammatically in Fig. 5.4. When air has bubbled gently through the soap and the compressed air supply is shut off, the column in the manometer balances the soap above the air orifice; and the manometer can be calibrated directly