OLEOCHEMICALS
FATTY ALCOHOLS

We will now look at Fatty Alcohols and how they fit into today's oleochemicals pipeline. As with most of the oleochemicals that have been covered in this booklet, we tend to be mildly surprised at where these chemicals turn up and how they affect our lives. Fatty alcohols are the workhorse raw materials that facilitate the existence of products such as shampoos, shaving creams, laundry detergents, etc, and are produced at a rate of about one-and-a-half million tonnes per year and growing.

WHAT IS A FATTY ALCOHOL?

We all know something about alcohol. The human race has waxed lyrical about various concoctions containing alcohol that have livened up many a party. Whisky (from the Gaelic Uisqe Beagh meaning water of life), contains about 40% alcohol as ethanol (ethyl alcohol). Alcohols occur as straight carbon chains with one or more hydroxyl (-OH) groups attached and, in exactly the same way as was outlined previously, there is a series of alcohol homologues distinguished by increasing carbon chain length.

Some examples which might be familiar are the aforementioned Ethanol, which has a 2-carbon chain; Octanol, where the carbon chain is eight carbons in length; Lauryl alcohol (dodecanol) with 12 carbons; Cetyl alcohol (hexadecanol) with 16 carbons and Stearyl alcohol (octadecanol) with 18. The lower chainlengths (C2-C10) are liquid at room temperature, whereas above C10 they vary from low melting colourless crystalline materials to white waxy solids (C16-C18), melting around 55°C. Those of you who take the time to read product labels in supermarkets cannot have failed to have encountered these materials in detergents, shampoos or cosmetics.

We will now focus a little more on the straight-chain alcohols generally produced from oils and fats. It is important to remember though that other types of alcohol exist. Production from petrochemicals gives rise to branched chain alcohols as well as straight chain species and it is also possible to have alcohols with more than one -OH, called polyhydric alcohols, much used in the manufacture of resins. A very important member of the last class is 1, 2, 3-propanetriol (or glycerine to most of us). This is such an important material in the oleochemicals industry that we will include a few words on its manufacture and uses later on. With the -OH at the end of the carbon chain, we get what is known as a primary alcohol and all of the materials we shall discuss fall into this category. With branched chain materials, the -OH can be surrounded by two or even three carbon chains, giving rise to secondary and tertiary alcohols respectively.

HOW DO WE GET ALCOHOLS FROM OILS AND FATS?

There are a number of ways that fatty alcohols can be obtained from fats and oils. Most involve reaction with hydrogen at high temperature and pressure and so require specialist plant to conduct the reactions safely. There are two main ways of working with fats and oils directly. Probably the oldest process is sodium reduction where metallic sodium is slurried in a solvent such as xylene and the triglyceride oil, a reducing alcohol (such as cyclohexanol) and more solvent are added to the reactor. The reaction occurs at about one atmosphere pressure and, in a second stage, the reaction mixture is dropped into water to hydrolyse the sodium alkoxides formed. The solvent and reducing alcohols are recovered by distillation for re-use and the by-product alcohol is generally fractionated to give the appropriate chainlength ranges commensurate with planned usage. This process has the advantage of retaining the unsaturation of the parent oil and gives very pure product. The disadvantages are high operating costs (due to the consumption of metallic sodium) and the elaborate equipment needed to recover both the solvent and the reducing alcohol.

Oils and fats can be converted directly to alcohols by hydrogenolysis in which process the triglycerides are hydrogenated at high temperature and pressure in the presence of specific catalysts. A mixture of fatty alcohols and glycerine results and, again, there is a significant amount of equipment and effort needed to separate these products before the alcohol is obtained and fractionated.

In a variation of the above process, called methanolysis, the triglycerides are reacted with methanol in the presence of a base catalyst. Fatty acid methyl esters and glycerine are formed and, after removing the glycerine, the esters are hydrogenated to make the alcohols which are fractionated as before. As methyl esters themselves have grown in importance, it is now possible to purchase these as the intended feedstock for hydrogenation and short-cut the process above with the advantage of not having to separate and deal with the glycerine. Similarly, triglyceride oils can be hydrolysed to fatty acids and the acids catalytically hydrogenated to alcohols and variation of catalysts and conditions can permit the retention of any unsaturation, if desired.

USES OF FATTY ALCOHOLS

Almost uniquely for oleochemicals, alcohols are sometimes less known by their common or chemical name, but more by their use. Thus, we often see the light-cut alcohols (C6-C10) called plasticizer range alcohols and C12-C18 known as detergent range alcohols. That gives us a clue to two of the major uses, but there are many more. Detergent uses in one form or other consume the largest proportion of alcohol produced. This usage depends on the ability of the alcohol to add fat-loving or lipophilic character to the detergent molecule. Alcohols are successful here and also provide, via the hydroxyl group, a reactive site which can add water-loving (hydrophilic) character of varying intensity depending on which chemical groupings get reacted into the molecule. This hydrophilic-lipophilic balance (or HLB) is key in identifying which detergents are good for removing fatty soiling and which remove non-fatty material. The HLB is generally modified through sulphation (reaction with sulphur trioxide in some form) to produce an alcohol sulphate, or through ethoxylation (reaction with ethylene oxide) to produce ethoxylates which can then be sulphated and used as is. These sulphates and ethoxylates are the active cleansing ingredients in laundry detergents, shampoos and shower gels.

In cosmetics and pharmaceuticals, we find alcohols being used as is because of their own specific properties, usually as emollients. For example, Cetyl (C16) alcohol is important in cleansing, shaving and vanishing creams, hair lotions, and lipsticks. Cetyl and Stearyl (C18) alcohol bring similar properties to antihistamine creams, bath preparations and dermatologic bases. Beyond this, fatty alcohols provide the starting point for chemicals used as defoamers, emulsion stabilisers, evaporation control agents, metal working lubricants, corrosion inhibitors, fire retardants, inks and perfumes - a wide-ranging (but still not exhaustive) list indeed.

GLYCERINE

No article on alcohols derived from fats and oils would be complete without a few words about glycerine. Glycerine occurs as a by-product of most of the reactions we have encountered as we have set out to make something else out of oils and fats. Hydrolysis, methanolysis and saponification all break the triglyceride molecule to yield glycerine. The glycerine accrues either as a 10-15% solution in water as a result of hydrolysis or as a consequence of washing esters or soap to remove the glycerine prior to further processing. This dilute solution is either quickly evaporated to 80%+ concentrations before being purified by distillation and carbon bleaching, or is pre-treated with lime to remove fatty impurities as insoluble soaps, before being ion-exchanged and distilled. The final product is water white and contains 99.5+% glycerine.

If we were surprised about the number and range of uses of the other fatty alcohols, those of glycerine will astound. It has been described as the widest used single high purity chemical in the chemical portfolio. Used primarily for its viscosity and humectancy, we find glycerine listed in mouthwashes, lotions, paints, plastics, baked goods, cosmetics, and pharmaceutical products, as both an excipient and an active ingredient. It might be easier to list where it is not used. With fatty alcohols selling for about 130 Euros/Kg and glycerine for about 0.7 Euros/Kg the value added to the parent fats and oils can be considerable.

Adding in the link to renewable resources, the minimisation of environmental impact due to the ready biodegradability of these materials and their potential for widespread use, it is easy to see that the alliance and partnership of the oil and fat producing industries with the technologies of the chemical industry is a very strong and potentially sustainable one whose products reach into every corner of our lives and, hopefully, will continue to do so.