

Synthetic Detergents

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THE word detergent means a cleaning agent. Further, it implies the removal of dirt or oily matter from a surface, usually, but not exclusively, a fabric. An example of a naturally occurring detergent is soapnut. Its limited occurrence and the economic aspects of its use prevent its universal applicability. Soap, as we know, is the alkali salt of a fatty acid and the first soap dates back to over two thousand years. The manufacture of synthetic detergents on a large scale is comparatively of recent origin. There is no hard and fast definition of the term synthetic used here. But for all practical purposes a synthetic detergent can be taken to mean a detergent where the carboxylic group of a fatty acid has either been blocked or modified by processes such as sulfation, amidation and esterification. The development of synthetic detergents has gained stupendous popularity during the last thirty years. This is mainly due to two factors. Fatty acid soaps are not suitable for use in hard water due to formation of calcium and magnesium salts of the fatty acids. Hence in an effort to develop a good substitute which had good detergency, Turkey-red oil was prepared. This was the first syndet (shortened name for synthetic detergents) to be produced. Further impetus to the development of syndets was given during the second World War due to a general shortage of natural fats, which are necessary for soaps. As a result, research work was stimulated in Germany, leading to a process for the conversion of fatty acids to sulfates by initial hydrogenation at high pressure. This was soon followed by American products of various types which flooded the market with unbelievable rapidity. At the present time, the task of reviewing or classifying all the synthetic detergents

is by no means an easy one.

A detergent is a balanced molecule made up of a nonpolar, hydrophobic hydrocarbon part with little or no residual valency and a polar or hydrophilic part with a high residual valency. The detergent solution in water is a colloidal electrolyte and is capable of micelle formation. The micelles are capable of occluding dirt or oily matter, a process technically termed as 'solubilization' of the dirt. The superiority of one detergent over the other consists in the efficiency with which it can accomplish this hold-up of dirt without redeposition, with as low a concentration of the detergent as possible.

Syndets are grouped into three main classes: (A) anionic, (B) cationic and (C) nonionic. Certain syndets exhibit the properties of both their anionic and cationic groups, when they come under the ampholytic group of syndets, a group which is not so well-known.

(A) Anionic Syndets:—

This is the most important group. Here the hydrophobic part is contained in the anion of the molecule. These are classified as follows:—

(i) *Paraffinic Chain Salt types*:— These were among the first to be developed and include sulfated fatty alcohols, alkyl sulfates and alkyl sulfonates.

1. Sulfate or sulfonate group joined directly to the hydrophobic group.

Examples: (a) Sulfated alcohol, where the hydrophobic group contains no other polar structures, (b) sulfated oils, where other polar groups are included in the hydrophobic part.

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2. Sulfate or sulfonate group joined through an intermediate link such as ester, amide, ether and other linkages.

Examples : (a) Arctic Syntex-M, which is the sodium salt of a sulfated monoglyceride, having the formula $R-COOCH_2CHOHCH_2OSO_3Na$.

(b) Xynomine, which is a sulfonated fatty acid condensate.

(c) Igepon AP, where the sulfonic group is attached through an ester linkage. The formula is $RCOOCH_2CH_2SO_3Na$.

(d) Igepon T, which is the sodium salt of the amide of oleic acid and N-methyl taurine. The formula is $CH_3(CH_2)_7CH=CH(CH_2)_7CONHCH_2CH_2SO_3Na$.

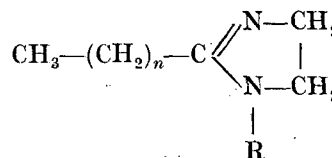
(ii) *Alkylated Aromatic Sulfonates or sulfates* :—Alkyl aryl sulfonates are the most important among the anionics, and are based on the dodecyl benzene, keryl benzene or dodecyl toluene structures as hydrophobic groups. Their general formula is $R-Ar-SO_3Na$, R being a fatty chain and Ar an aromatic group, an example being di-isopropyl naphthalene sodium sulfonate. Other examples are: (a) Triton X-770, which is the sodium salt of alkylated aryl polyether sulfate, (b) Alkyl phenols, where hydrophobic group is joined directly to sulfonated aromatic nucleus and (c) Sulfophthalates, sulfobenzoates, sulfobenzamides and sulfobenzimidides, where the hydrophobic group is joined to the sulfonated aromatic nucleus through an intermediate linkage.

B. Cationic Syndets :—

Here the hydrocarbon portion of the molecule is present in the cation part and acquires a positive charge on ionisation. The two classes in this group are (1) the amine salts and (2) the quaternary ammonium compounds. The

cationic syndets are known more for their use as germicides than as detergents. The compound named 'Sapamine' in the trade is an amine salt. It is prepared by heating oleic acid with unsymmetrical di-ethyl ethylene diamine. It has the formula, $CH_3(CH_2)_7CH=CH(CH_2)_7CONHCH_2CH_2N(C_2H_5)_2$. Sapamine can foam in concentrations as low as 1:2,000,000.

Alkaterge is another example of an amine salt, where the amino group is a part of a heterocycle. It is a substituted Oxazoline. Alro Amines are heterocyclic tertiary amines having the general formula.



Dimethyl lauryl benzyl ammonium chloride and cetyl pyridinium chloride are examples of detergents belonging to the quaternary ammonium compounds. Compounds such as Zelan, Velan and Norane which are alkyl pyridinium salts are used in textile fibre processing. In contrast to the anionic class, cationic syndets are extremely effective and quite stable in acid solutions.

(C) Nonionic Syndets :—

Nonionics were first developed for use in the form of sulfonated oils and reach back to over a hundred years. In the thirties of the present century, a compound called Igepal CA, which is the ethylene oxide condensate of an alkyl phenol, was brought forth by the Germans. The German government gave an impetus to their development, since the products were fat-free, thus attempting to make their country self-sustaining with respect to fat requirements.

The detergents of this class are composed of a nonpolar unit usually derived from fatty acids, fatty alcohols, alkyl phenols or mercaptans combined with a polar group usually a polyethylene glycol chain introduced into the structure by condensation of ethylene oxide with the hydrophobic base. The properties of the nonionics are entirely dependent on the equilibrium between the polar and nonpolar units. A low contribution of ethylene oxide to the hydrophobic base usually gives a liquid product, while larger components result in the product becoming pasty or solid, due to an overbalance in the direction of the hydrophilic portion of the molecule. However, by proper choice of the hydrophobic and hydrophilic parts, the degree of activity of the detergents can be varied at will.

At present, the nonionics are becoming increasingly popular from day to day, since the process of their manufacture is relatively simple. Also the nature of the process is such that the product contains very nearly 100% active agent, thus being essentially free of contaminants and diluents. Due to increased production and improved manufacturing techniques nonionics have become more cheap and are successfully competing with the nonionic detergents.

Examples of nonionics are:

Polyethylene ether of lauryl alcohol,

Polyethylene ether of 1,1,3,3-tetramethylbutylphenol, and mannitan and sorbitan esters of higher fatty acids and polyethylene oxide derivatives thereof. Mention may be made in passing of the ampholytic class of synthetic detergents. These exhibit properties of both anionic and cationic groups. However, very few ampholytic detergents have reached commercial importance. The amino, carboxy and sulfuric esters are representative of this class. The sulfuric ester ampholytes are prepared by sulfating hydrophobic amines containing either

an olefinic double bond or a hydroxyl group. The carboxy acid ampholytes are prepared by reacting higher alkyl amines with halogenated carboxy acids. The past several years have witnessed three important developments in the syndet field:

1. Introduction of heavy duty type synthetics carrying such builders as the poly and pyrophosphates. A builder is added to a detergent to improve its performance and not as a diluent. It provides satisfactory detergency at a reduced detergent concentration.

2. Use of carboxy methyl cellulose (CMC), especially with the alkylaryl sulfonates, to improve detergency with cotton. CMC is present in this anionic detergent to the extent of 3%.

3. Increased use of alkyl aryl sulfonates in place of higher priced fat-bearing materials such as the sulfated mono-glycerides and the sulfated alcohols.

Detergents and Foaming Power:—

A good detergent is almost always associated with a good foaming power. Foams perform one of the vital operations so necessary for cleaning, i.e., wetting when bubbles or a gas are dispersed more or less stably in a continuous liquid phase, the resulting system is called foam. The conditions favourable for the formation of foam are low surface tension, low vapour pressure and the presence of a surface active agent. The foaming power increases with surface activity, or, to put it in other words, colloidal aggregation diminishes the chance of foam formation. Foaming powers of soaps from natural fats decrease in the order, palm, oil tallow—coconut oil.

Unfortunately, though syndets attain maximum detergency at low concentrations, they have low foaming power at

such concentrations. Furthermore, soil has a defoaming action on them. Saunders and Knaggs report that alkylo-lamides can successfully be used to stabilize the foam of synthetic detergents.

Soaps Versus Syndets :—

The battle between the natural and the synthetic has been on now for many years and has now reached a critical stage. Figures released by the American Soap and Glycerine Producers Inc. shows that for the 3 months ended March 1953, sales of syndets represented 53% of the industry's total soap and syndet sales. This is hardly believable in the face of the fact that in 1930 soap had the sole monopoly. The fear that fatty acid soap may one day vanish from the surface of the earth has been expressed by many. However, for the soap manufacturer, there are still good grounds for being more optimistic than ever. Here are some points which are in favour of the soap industry.

(a) *Raw Materials* :—Some of the important raw materials for syndets are benzene, caustic soda, catalysts like hydrofluoric acid, aluminium chloride, sulphuric acid and copper chromate, ethylene oxide, hydrogen, paraffin, kerosene, propylene, sodium, polysulfates and vegetable oils. It is estimated that with the present rate of output of syndets, raw materials will be sufficient only for about 5-6 years, materials in short supply being benzene, sodium and sulphur.

(b) *Cost factor* :—1 lb. of active synthetic detergent costs about 5 times as much as fatty acid soap. The average household syndet contains about 20% of the active detergent as opposed to about 60% in a fatty acid soap. Still, fatty acid soaps are cheaper. Moreover, while 1 lb. of a syndet requires a third of a pound of sodium hydroxide, only one-eighth lb. of sodium hydroxide is sufficient for soap. Also the syndet indus-

try has grown into a heavy chemical industry, involving industrial operations such as sulfonation, sulfation, handling of petroleum and the like. The syndet industry has further been the indirect cause of the rise in prices of glycerine. It should be remembered that unlike the fatty acid soap industry, glycerine is not a by-product in the syndet industry.

(c) The average syndet does not favourably compare with soap in detergent power when used under conditions ideally suited for the maximum efficiency of soap. Furry and co-workers have shown that syndets are less effective in distilled water than the soaps.

(d) *Dermatitis* :—This is the name given to the reddening of the skin produced by the use of syndets. This has been explained as due to the formation of an emulsion with the protective grease layer over the skin by the detergent, thus rendering the skin rough. Though this reflects on the too good properties of the syndet, it may well affect the future of synthetic detergents.

(e) *Sewage Disposal* :—While more and more of syndets are being used in America, the problem of sewage disposal is taxing the chemist and the sanitary engineer alike. Firstly, the sewage pipes get corroded by the detergent solutions entering the drains. Secondly it is very difficult to settle the sewage containing these detergent solutions.

Manufacture in India :—

Manufacture and introduction of syndets into the market in India will take some more years. This is mainly because of the fact that the need for syndets will have to be felt before a plant is set up here and for this to come, we must boost up our *per capita* consumption of soap, which being the lowest in the world, stands at 0.4 lbs.; compared to 28.7 lbs. in Belgium. This calls for more of publicity and a strong

advertising campaign for soaps, from the Indian detergent manufacturer.

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Synthetic Fibres and Their Future

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A TEXTILE fibre is defined as a "slender filament or fine strand of sufficient length, pliability, and strength that can be spun into yarns and woven into cloth." Fibres are distinguished from filaments in that, the latter are processed fibres of continuous length, most conveniently measured in yards or meters, while the length of fibre is usually given in terms of inches or centimeters. Both single or mono-filaments and multifilaments are known. Fibres and filaments, can either be inorganic or organic but from the point of view of textile fabrics only the organic ones are of major importance. These organic fibres are composed of chain molecules, the fibre in its macro-structure being the reflection of its own micro-structure, as has been shown from X-ray studies of fibres by Astbury, Chibnall and other.

Textile fibres may be broadly divided into the divisions, (1) natural fibres and (2) man made or synthetic fibres. The more important natural fibres can be

again classified into two groups (1) cellulose fibres (e.g. Cotton), and (2) protein fibres (e.g. Wool and Silk).

Typical cotton fibre contains 90% cellulose, 80% moisture, 1% mineral matter, 0.5% wax and fats, 0.4% pectic substances. Cellulose is a polymer of β -anhydroglucose, the various monomeric units being linked by 1-4 bridges. In cotton there is a high degree of crystallinity (60 to 70%), that means a predominant preferred orientation in which the molecules are lined more or less parallel to the axis of the fibre, resulting in ease of spinning. Cellulose is also found in wool, grass and other structural cell-walls of plant materials; however, it cannot be directly spun into fibre as in addition to cellulose, it also contains appreciable amounts of non-cellulosic materials which can be removed by treatment with sodium hydroxide, sodium sulphide, calcium bisulphite etc., and subsequent bleaching. The purified cellulose so obtained can

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