CHAPTER II

REVIEW OF LITERATURE

The relevant literature have been reviewed in this chapter. Related information from pamphlets/leaflets provided by manufacturers of commercial washing machines has also been presented.

The literature has been categorized into the following subsections :

2.1 Soaps and synthetic detergents, their classification, general properties and applications

2.2 Principles of laundry and present trends in laundry compositions and their combinations

2.3 Research studies in soiling and detergency

2.4 Recent trends in washing machines.

2.1 Soaps and synthetic detergents - their classification, general properties and applications

The molecules of a surface active compound are not distributed uniformly in an aqueous solution. They tend to congregate at the surface. The hydrophobic tails are repelled by water and the molecules tend to arrange themselves with their tails emerging. At the interface a reduction in surface tension is caused by the tendency of hydrocarbon chains to move away from the water phase and it creates a force in the direction opposite to the inward pull of the water molecules.

A simple classification has been given by Martin and Fulton (41) as soaps and other than soaps :

a) Detergents based on soaps as active ingredients are of three types : paste-type, gel-type and liquid-type

b) Detergents other than soaps are synthetic detergents as anionic, cationic and nonionic.

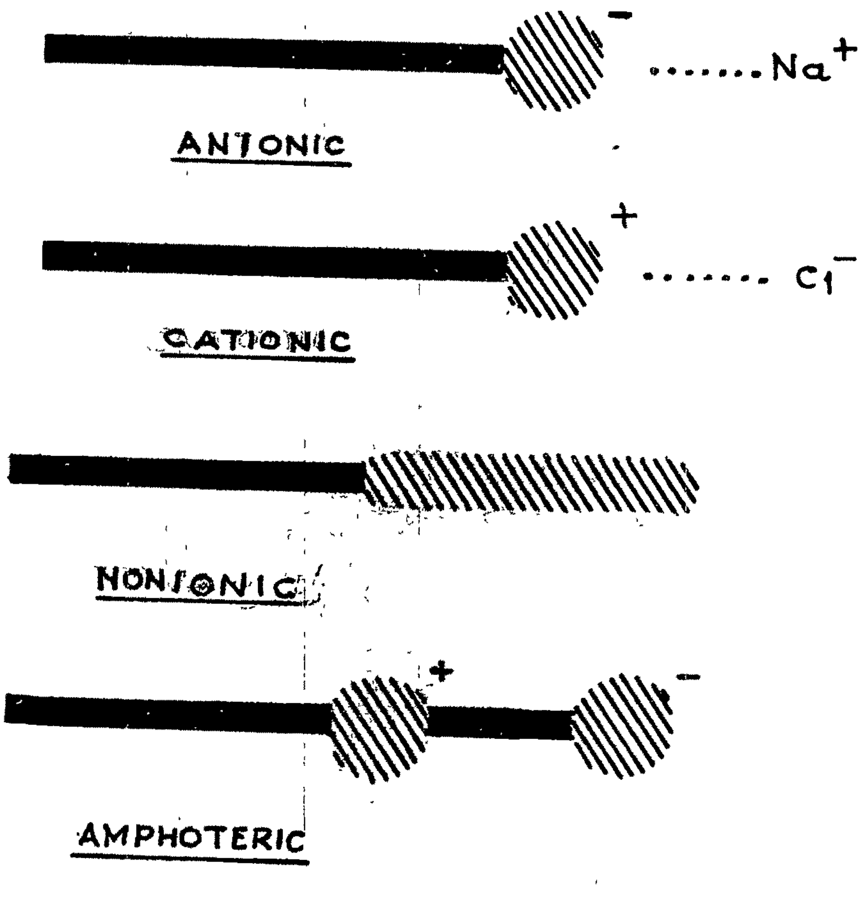
As given by Cross (15) surfactants can also be classified as soft and hard, soft are biodegradable and hard are nonbiodegradable.

Soaps and synthetic detergents have been classified by Grantz (29) into four groups according to their ionic behaviour : a) anionic, b) cationic, c) nonionic and d) amphoteric. A schematic representation of these is shown in Figure 1.

Anionic molecules bear a negative charge and migrate towards the anode in solution. Cationic molecules show the opposite behaviour as they contain a positive charge. Nonionic surfactants do not contain an ionizable group and so have no electrical charge. The hydrophilic end of this type of surfactant is usually made up of several hydroxyl groups or other linkages. The hydrophilic part of a nonionic molecule is usually larger than that of anionic or cationic and may even be much larger

FIG. 1

SCHEMATIC REPRESENTATION OF SURFACTANT TYPES



than the hydrophobic part of the molecule. Amphoteric surfactants contain both a positive charge and a negative charge. These charges may neutralize each other so that at a given pH, the surfactant behaves as if it were nonionic. These surfactants usually exhibit cationic properties in acid solutions and anionic properties in alkaline solutions.

This system of classification has been shown in Table 1 and it includes most structures that are commercially significant. These have also been shown schematically in Figure 2, 3, 4, 5, 6.

General properties and applications

The most important property of surface active agents is to lower the surface tension and detergency is closely bound up with low surface tension.

Molliet and Collic (47) suggest that the surface active molecules of ions can be looked upon as a bridge between the two phases making the transition between them less abrupt. The crowding together of molecules at the interface gives a closely packed boundary layer, offering resistance to the liability of the surface to diminish the area. A surface active compound thus tends to lower surface tension at boundaries between water and air or oil.

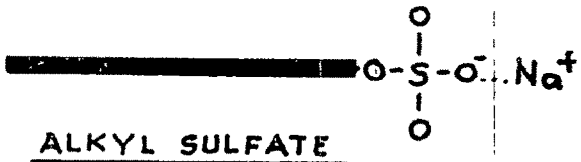
The correlation between lowering of surface tension and improved detergency was found by Cronin and coworkers in their

Table 1. Classification of surfactants

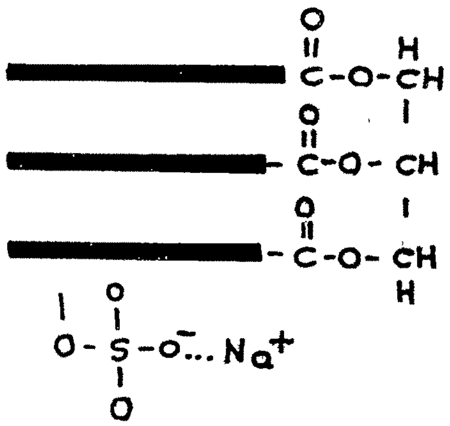
Anionics	Cationic	Amphoteric	Nonionic
A. Carbolic acids:	A. Simple amine salts	A. Amines plus carboxyl or sulphonic ester group	A. Alkyl, alkylaryl and thio esters
1. Soaps, fatty acids, rosin and naphthelene acid	B. Quaternary ammonium salts		B. Esters and amides
2. Miscellaneous	C. Amino amides and Imida-zolines		C. Miscellaneous
B. Sulphuric acid esters:			
1. Alkyl sulphates	D. Amine oxides		
2. Sulphated oils	E. Amphoteric		
3. Sulphated esters, esters and amides			
4. Miscellaneous			
C. Sulphonic acids:			
1. Alkyl			
2. Alkyl aryl			
3. Sulphonated amides acid esters			
D. Phosphate esters:			
1. Mono di triesters			
2. Miscellaneous			

FIG. 2

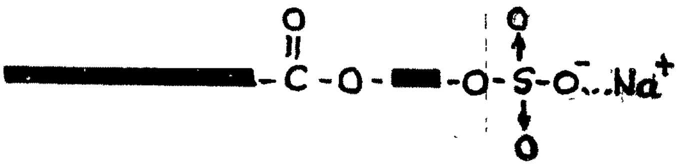
SULFATE ESTER SURFACTANTS



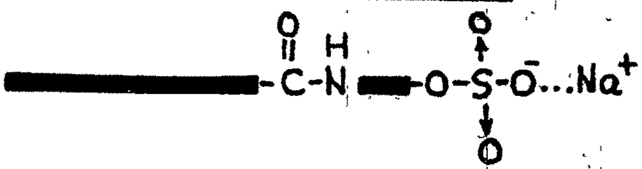
ALKYL SULFATE



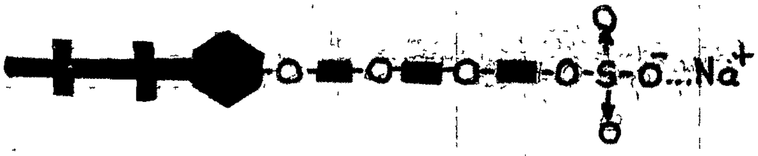
SULFATED OIL OR FAT



SULFATED GLYCOL ESTER



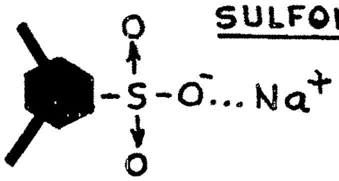
SULFATED ALKANOLAMIDE



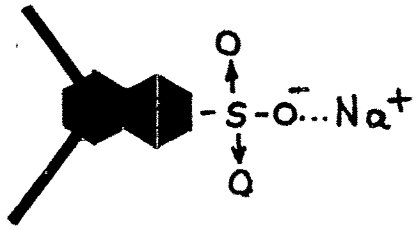
SULFATED ALKYLPHENOL POLYGLYCOL

FIG. 3

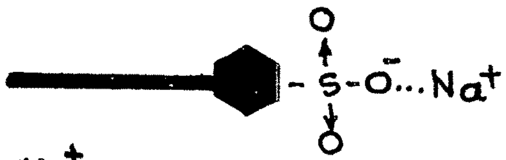
ALKYL AND ALKYL ARYL SULFONATES



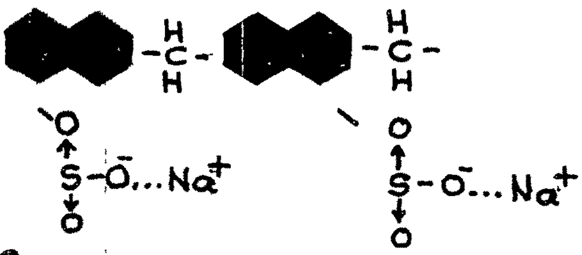
SODIUM KYLENE SULFONATE



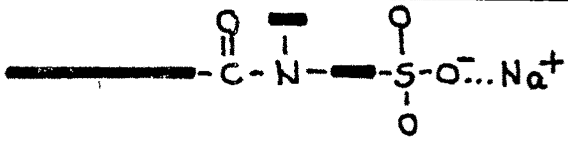
SODIUM DIBUTYL NEPTHALENE SULFONATE



SODIUM DODECYLBENZENE SULFONATE



SODIUM SULFONATE OF NEPTHALENE FORMAL-DEHYDE CONDENSATE



SULFONATED AMIDE

FIG. 4

MONO, Di AND Tri-PHOSPHATE ESTERS

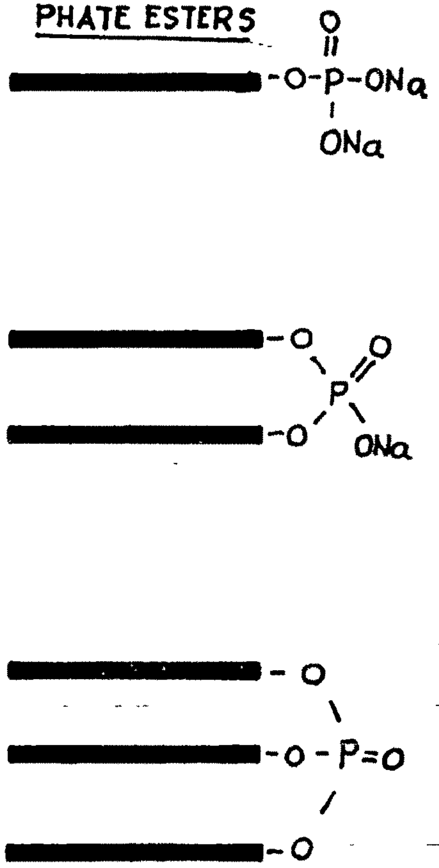


FIG. 5

CATIONIC SURFACTANTS

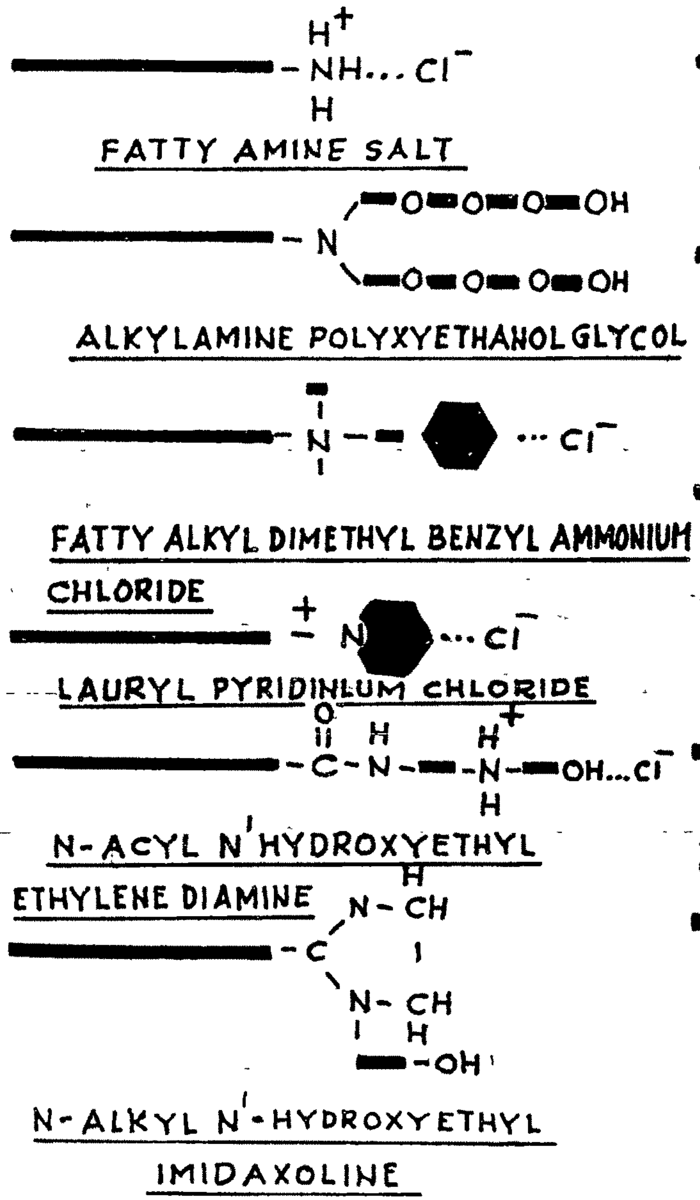


FIG. 6

AMPHOTERIC SURFACTANTS

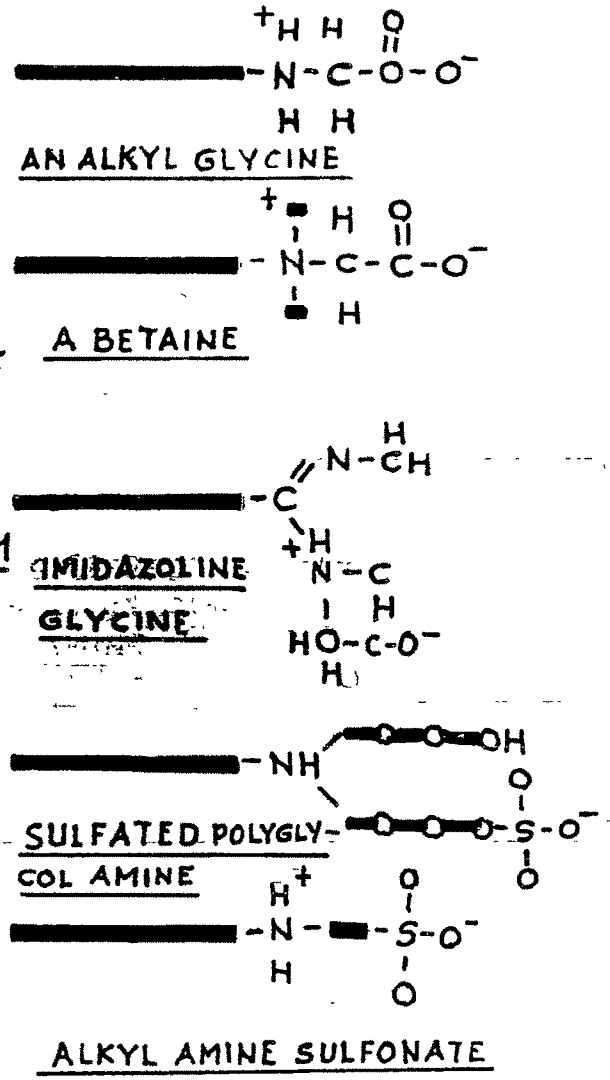


TABLE - 2

FUNCTIONAL USES OF VARIOUS SURFACTANTS IN TEXTILE PROCESSING

	WETTING	EMULSIFICATION	DETERGENCY	DYEING	SOFTENING
ANIONICS					
SOAPS			X		
ALKYL SULFATES	X		X	X	
SULFATED OILS		X		X	X
ALKYL ARYL SULFONATES	X		X	X	
SULFONATED AMIDES	X		X	X	
PHOSPHATE ESTERS		X			
CATIONICS					
QUATERNARIES				X	X
AMINO AMIDES ETC.				X	X
OXYETHYLATED AMINES				X	
AMPHOTERICS					X
NONIONICS					
ALCOHOL BASE	X	X		X	
ALKYL PHENOL BASE	X	X	X	X	
ALKYLOLAMIDES	X		X	X	

work on nonionic detergents. Between 12 to 14 ethylene oxide linkages, correlated well with maximum detergency. The hydrophyll-lipophyll balance values must be controlled to provide optimum detergent effectiveness. If the hydrophobic portion of the molecule is small the detergency will be correspondingly reduced. The optimum soil removal values seem to be obtained when a nonionic detergent is used close to its cloud point.

A detergent cannot be reduced to a single measurement such as measuring how much the compound lowers the surface tension of water or how much foam it produces. A surface active agent which markedly lowers the surface tension of water is not necessarily a detergent because many substances that do so, have no cleaning properties at all.

None the less, the foam is a better criterion of cleaning power than the lowering of surface tension as the foam has an important role in the removal of dirt. It also acts as an indicator of the life of the detergent during cleaning. But unfortunately not all that foams is a detergent and it has been proved that poor foamers may be the basis for outstandingly effective detergent compositions.

Limited correlations have been pointed out between foaming and other properties. Molliet (47) has shown that in the three series R SO_4Na, R SO_3Na and R COONa, the minimum concentrations necessary to produce foaming is relatively independent of temperature and foaming decreases as the chain length increases. The rate of foam build up was found to vary with chain lengths in these series. Similar effects for various other series compounds and mixtures have been reported but without any specific generalization.

Low foam formulations have been based on mixtures of nonionics with soaps, tallow alcohols, sulphates and other ionics. It is also noteworthy that certain anionic detergents of tatride series are essentially low foamers but very effective cleaners (47).

No direct correlation between foam and detergency has been noted. In general nonionics are relatively low foamers as compared with anionics, whereas their detergency properties seem to be superior to those of anionics (47).

Studies on foam density using aqueous solution of soap have shown that micelle formation has a marked effect on foaming. Below the critical micelle concentration, the foam density like the surface tension is proportional to log of the bulk concentration. Above the critical micelle concentration the foam density is relatively independent of bulk concentration. These relationship appear to hold for the synthetic detergents like Teepol as well as for soaps (47).

Early investigations have noted the dependence of optimum detergency upon concentration, however Preston's (39) work has now shown that detergency and critical micelle concentration are related. A micelle is a group of molecules associated in a cluster from which the more mobile ions have migrated leaving a net charge of the opposite sign on the cluster (56). Washing power is at its maximum at critical micelle concentration. The peak break in detergency curve did not necessarily coincide with critical micelle concentration to clarify this correlation. Removal of radioactive soil was found by Chandler and Shelber (39) to begin with micelle formation and to increase rapidly when micelle concentration was two or three fold that of concentration. Demcheulo (39) varied the practical significance of concentration but claimed that soil removal started only when detergent concentration was in excess of critical micelle concentration. The importance of this value to soil removal therefore is well recognized and recent work suggests that while the optimum removal occurs at concentration in excess of critical micelle concentration, systematic investigation to fortify these opinions has not been available.

An account of the factors determining the critical micelle concentration of nonionic surfactants has been given by Scott (15). The main difference between nonionic and other detergents apart from overall detergent efficiency lies in the differing concentration at which maximum detergency is achieved. The optimum results at lower concentration with nonionic surfactant is attributed to the very low micelle concentration of nonionic surfactants. On the basis that lower concentration values indicate surfactant activity at lower concentration level, knowledge of the controlling factors have both high economic and quantitative values.

Data for many surfactants over a wide variety of conditions has been published (15). For a given alkyl chain critical micelle concentration increases in the order nonionics $<$ zwikerionics $<$ ionics (anionic and cationics).

Although the ability to wet out soils and substrate is important for detergency, however effective detergents as measured by soil removal are not necessarily the best wetting agents for the detergent system as such. An extensive search of the literature developed valuable information relating wetting power to concentration, surface and interfacial tension, contact angle, critical surface tension of the solid and others, but none of them were strongly correlated with soil removal.

Burick (37) studied the rate of surface tension lowering and its role in foaming. Surface tension was measured as a function of these by the dynamic method of addition for aqueous solutions of sodium laurate. The stability of foams was judged by measuring the average life of a single bubble and also half life of foam. The solutions having high foam stability are those with low surface tension, high surface viscosity and moderate rate of surface tension lowering.

2.2 Principles of laundry and present trends in laundry Composition and Combinations:

Soil on textiles is complex and consists of dirt of varying origin, body secretions (mainly skin fat) and several organic and inorganic contaminants from industrial and domestic activities. By definition (34) soil is a mixture of oily and fatty contaminants with solid pigments.

Removal of oily soil is based on (a) wetting and rolling up for which quantitative relationships have been established, (b) solubilization which is particularly with nonionic surfactants, (c) emulsification and (d) the formation of mixed phases. During the washing process a limited time span is available for the consecutive steps of wetting, adsorption and soil removal to take place. Hence at many interfaces equilibrium can be reached before the process is stopped.

Mechanisms of detergency are discussed from the kinetic point of view. In general soil removal involves (a) an induction period during which soil removal is slow, (b) a rapid soil removal period during which the amount of soil in the substrate decreases linearly with the increasing logarithm of the washing time and (c) the final period during which the amount of soil retained does not decrease significantly (34).

The rate of water diffusion rate into soil-release fabrics does not always correlate with actual soil removal. Soil removal is either spontaneous or requires mechanical work, resulting in hydrodynamic flow, cavitation flexing of the fabric etc. Spontaneous release of oily soil is related to absorption and diffusion of water in the swollen fibers or soil release polymer and hydration of the interface polymer.

Conditions required for laundry

To get effective cleaning three steps must be accomplished (55) :

a) The aqueous phase must wet the surface of the fibre,
b) The dirt must be detached from the fibre and
c) A stable emulsion must be formed so that it will not be redeposited.

Dirt is held to the surface of any material by mechanical, chemical or electrical force. The material that usually binds the dirt is greasy and grease repels water. The detergents help in weakening the bond between the surface and the dirt. This is done by another force and that is surface tension. Surface tension causes the liquid to expose the minimum surface area possible to the atmosphere so the wetting power will increase with the reduction of surface tension. For cleansing, water is the most commonly used liquid but it has a low wetting power so to increase wetting power detergents have to be added to the water. The detergent molecule is shown as micelles. In water the hydrophobic tails push themselves out of the water surface. This reduces the surface tension. The globular structure of the water drop now collapses and the drop spreads. This in turn exposes a greater surface area to more detergent molecules. This process continues, more detergent molecules stick out these tails at the water surface and the water spreads all over. It thus increases the wetting power.

Fava and Eyring drew attention to the importance of adsorption of the detergent by the fabric and suggested that the essential step in laundry were :

Fibre/Dirt + Detergent = Fibre/Detergent + Soil/Detergent.

Detergents also help remove the dirt particle by lifting it bodily. The hydrophobic tails have an affinity for dirt particles. They fix themselves to the dirt on the soil surface. This creates a clearance or a space between the dirt and the soiled surface. More water and detergent enter the gap and the dirt is completely separated.

The detached granules will be covered with a surface film of detergent molecules. The charges on the droplets will cause mutual repulsion, keeping them uniformly distributed throughout the aqueous phase as a stable emulsion. The most important step in detergency is the dislodging of the dirt molecules from the fabric. Vigorous agitation in water alone will remove some of the dirt, but the presence of a detergent brings about detachment with much less violent effort. The efficiency depends very much upon the nature of the detergent (18).

Though there are numerous makes of household power washing machines in the market, differing in the means employed to move the clothes, or water or both, The underlying principle is the same - namely that for maximum cleansing, the dirt must be loosened from the fabric by the combined action of detergent and water and by the mechanical movement of the soiled clothes through water. There are many different principles used for agitation which are discussed later.

Present trends in laundry compositions and their combinations

The soap and detergent industry is vast. World production in 1984 was 24.36 million metric tonnes.

The first synthetic detergents were introduced in the year 1930 in areas where water hardness and mineral contents were the highest and the resulting soap curd problems were severe. The detergents were anionic -- first sulphated alcohols and later sulphonated alklylbenzenes. As detergents continued to spread from hard water areas to regions with soft water and less soap curd occurrence. The anionics have strong rich lather, a characteristic that consumer already associates with cleaning efficiency. And they were indeed, efficient cleaners of fabrics found in the average wash-load, cottons by and large. In 1950 for example cotton accorded for more than 70% of the world's production of textile fabrics with synthetic fibers at about 18% and wool 10%. By 1964 synthetic had started a serious growth accounting for about 28% of the world production textile fabrics. Cotton's share had begun shrinking hitting about 62%. Seven years later cotton was down to 60% and synthetic fabrics had jumped to 40%. Detergent makers noted that as good as the anionics were at cleaning cotton, the nonionics were better at cleaning the synthetic fibers, and the rise in consumption of nonionics started to follow that of new fibers. Another plus point for the nonionics was a better resistance to hard water ions than the anionics, which helped them more into formulations when phosphate bans began hampering detergent efficiency. Since nonionics are easier to incorporate into liquid detergents than are anionic surfactant, they got a boost when liquid heavy duty detergents began their dramatic rise in popularity in the mid to late 1970's from 4% share in the market in 1970 to now just less than 20% of the heavy duty detergent market (33).

Though India is the 2nd largest producer of soap in the world it has the lowest per capita consumption. At present we consume 2.3 kg per capita per annum as against 14 kg per capita per annum in USA and 12 kg per capita per annum in West Germany. Further our consumption is concentrated in the urban areas, while our vast rural population remains relatively untapped.

Our total demand for washing products by 1990 has been estimated at22,25,000 tonnes of this 9,10,000 tonnes will be washing soap, while 1,315,000 tonnes are estimated to be chemical detergents (1).

In today's society, choice of a commercial detergent product for laundering of garments, necessitates consideration of the twin factors of good washing and cost. In general, the aim is achieved by using a typical detergent formulation as given below :

adequate amounts of active detergents (AD),

a sequestant (STPP) for the removal of hardness ions such as Ca^{++}, Mg^{++}, Mn^{++} and Fe^{++},

soil releasing agents, optical brightners, and

moderate amounts of alkali (soda ash).

On the other hand, since the sales appeal of a cheap, detergent product is its low price, none of those wash benefit ingredients is used in such a product but instead very high amounts (50%) of alkali which have little relevance to cleaning but may actually make the detergent product harsh on fabric (8). It was seen in the study by Pradhan (43) that harshness will produce early wear and tear of garments and may perhaps nullify savings effected by using the cheap detergent product.

The Bureau of Indian Standards (BIS) has formulated standards and has classified them into four grades depending upon the percentage of active ingredient present in them. Detergents with 19 per cent active ingredient in them are in grade one, while those with 16 per cent of active ingredients belong to grade two. Grade three and four detergents have 10 to 12 per cent of active ingredient in them respectively. Experts feel that since the active ingredient is one of the major components of a detergent it should be mandatory for all detergent manufacturers to specify the grade as per ISI specifications or indicate the name and the percentage of active ingredient and builders used on the package. Such a move would also curb the tendency of some manufacturers to reduce active ingredient, to eliminate phosphate builders altogether and to increase the soda ash content instead. This may considerably reduce the price of detergent, but it also decreases its cleaning efficiency and will eventually harm the clothes as well as the hands of the users (28).

Anionic surfactants are commercially the most important representing about 50% of the total surfactant production. Typical common examples are :

1) Soaps
2) Salts of sulphated esters of fatty alcohol and
3) Alkylbenzene sulphonates

$$\underset{(1)}{C_{17}H_{35}COONa^+} \qquad \underset{(2)}{C_{12}H_{25}OSO_3^-Na^+} \qquad \underset{(3)}{C_{17}H_{25}C_6H_4SO_3^-Na^+}$$

As indicated, anionics surfactant are to be found in a variety of consumer products. For example in a formulated (or built) laundry detergent one would expect to find an anionic surfactant mixed with:

(a) Sodium salts such as poly and monophosphates, nitriloacetates ethylene diamine tetra acetate, silicates and carbonate performing a variety of functions such as binding the surfactants into a free pouring powder, controlling pH, increasing the ionic strength, preventing corrosion and complexing calcium and magnesium ions.

(b) Antidesposition agents, such as sodium carboxy methyl cellulose.

(c) A flourescent optical brightner and

(d) Sodium percarbonate or perborate as a bleaching agent (15)

According to Alter (6) a so-called heavy duty home laundering detergent may contain as many as six or nine separate ingredients. The major ones are surfactants (10.2%) and sodium tripolyphosphate (30-50%) other ingredients provide anti-redesposition (Carboxymethyl cellulose) Corrosion protection (Sodium silicate), alkalinity (washing soda) brightner and fillers (sodium sulphate).

Bisltine and Striton (10) stated that the function of the phosphates builder is not completely understood. The phosphate builders act as sequestering agents for the Ca^{++} and Mg^{++} of hard water, as a source of buffered alkalinity and they affect the miscellaneous properties of the detergent. They also stated that they are able to remove soil to some extent and may have some desirable colloidal properties of their own to contribute to the washing process. In their study of the reduction of phosphate builders in tallow based detergents formulation they found that when the active ingredient was an anionic (based upon hydrogenated tallow alcohol sulphate or linear alkyl benzyne sulphonate) and the cotton cloth manufactured by test fabrics was more hydrophillic in composition (due to the presence of aromatics, cellulosics and emulsifier as soiling agents). The phosphate builders could be halved (.04%) without loss in the detergency. A slight decrease in detergency was observed for this same detergent when the phosphate builder was reduced if the cotton fabric was soiled with carbon, high molecular weight hydrocarbon and fatty oils.

The washing behaviour of various mixtures of common household detergents ingredients is a rather frequent subject of publication. It is well established and widely acknowledged fact that soap is generally superior to any of the common synthetic in the absence of builders and in soft water. Even in hard water, soap will out-perform the synthetics if the soap concentration is sufficiently high to take care of hardness (47).

Table 3 Composition of common detergents in West Germany (1981) (58)

Substance	Examples	Type of Detergent		
		Heavy duty detergent	Detergent for washing at 60°C	Special detergent
Anionic or nonionic surfactant	Alkyl benzene sulphonate, alkane sulphonate, alkyl sulphate, polyglycol ether	10 - 15	10 - 15	15 - 25
Complex former, ion exchanger	Sodium triphosphate Na AI silicate	30 - 40	40 - 65	15 - 30
Bleaching agent	Sodium perborate	15 - 30	0 - 15	-
Greying inhibitor	Carboxy methyl cellulose, cellulose ether	0.5 - 2.0	0.5 - 2.0	0.5 - 2.0
Corrosion inhibitor	Silicates	3.0 - 6.0	2.0 - 6.0	0.2 - 6.0
Stabilizer	Magnesium silicate	0.2 - 2.0	0.1 - 2.0	0.0 - 0.2
Foam inhibitor	Special soaps or silicone soaps	0.1 - 4.0	0.1 - 3.0	0.1 - 2.0
Perfumes		0.1 - 0.3	0.1 - 0.3	0.1 - 0.3
Fillers	Sodium sulphate	5 - 20	5 - 20	15 - 20

Mixtures of soaps with various synthetic detergents have been studied by many different investigators. Some of the synthetic detergents such as the fatty alkylolamide, have been used as additives to upgrade the performance characteristics of liquid soaps. The wetting power of soap, which is poorer than that of the better synthetics, is greatly improved by the addition of relatively small proportion of lauryl sulphate or alkyl lauryl sulphonate. Mixture of soaps with alkyl aryl sulphonate have been studied by Hetty Morgan and coworkers (47). These mixtures appear to retain many of the desirable properties of each component and therefore are more versatile than either component taken separately. Teepol soap mixtures are improved if the soap is formed <u>in situ</u> by treating a Teepol acid-fatty acid mixture with alkali.

Mixture of alkyl aryl sulphonate with carboxy-methyl cellulose have been studied by Vaugh and coworkers (47). These investigators have found that the mixtures possess as much as 50-100% greater detergent power (under special conditions of water hardness, soil etc.) than pure alkyl aryl sulphonate. Sodium carboxymethyl cellulose has a favourable effect on mixtures of soap with alkyl aryl sulphonate but the effect is less pronounced than it is in the case of alkyl aryl sulphonate alone.

Although most of the information on surfactant mixtures with soap is found in the patent literature some detailed review on individual mixtures are available. Flett, Morgan and Hoyt have described the behaviour of mixture of soap with dodecylbenzene sulphonate particularly from the view point of compounding and the advantages to be expected in various detersive application. A similar view on the blending of mersolates with soaps has been published by Groninger

In both these instances the emphasis is on bar forms, and the advantages secured from the soap is that a satisfactory bar can be obtained. The synthetic detergent component contributes the hard water foaming, wetting and washing performance.

Reuteuaner, Prelat and Sicard have studied the foaming, wetting and emulsifying power of a standard tallow soap mixed in varying proportions with anionic detergents dedecylbenzene sulphonate, noxylnaphthalene sulphonate, Teepol (secondary alkyl sulphate) and oleyl sulphate. A nonionic polyethenoxyalkyl phenol ether was also included in the study. In general, the desirable properties of each component were conserved in the mixture. Thus the synthetic detergent contributed foaming and wetting power in hard water whereas soap contributed the good emulsifying power which is lacking in some of the above named types.

Mixtures of soap with the sulphated oils and sulphated fatty acids have been used as nonirritating cleansers. They are effective in hard water if sufficient sulphated component is present. The sulphated oils are noted for their mildness towards the human skin although their cleansing power is not particularly high. In this case cleansing power is supplied by the soap.

Mixtures of soap with the Kritchevsky type fatty diethanolamide detergent have been used to a considerable extent. The synthetic detergent in this case acts mainly to modify the foaming properties and as a lime soap dispersing agent. The polyethenoxy nonionics are, in general, excellent lime soap dispensers and have been used, in minor proportions relative to the quantity of soap present for this purpose. Larger proportions of these nonionics have been mixed with soap to form low foaming detergents suitable for use in mechanical washers.

One of the most widely used mixtures in the surfactant field is the mixture of a fatty alkyl sulphate with an alkyl aryl sulphonate. This mixture is prepared with a suitable proportion of each ingredient is difficult to distinguish from an unmixed fatty alkyl sulphate, particularly with regard to foaming and detersive properties. It has consequently been used in household detergent composition to replace the more expensive fatty alkyl sulphate. The mixture of alkyl aryl sulphonate and fatty alkyl sulphate also have greater solubility than either components used in the preparation of liquid detergent compositions.

Mixtures of the ampholytic detergent dodecyl beta amino propionic acid with alkyl aryl sulphonate are claimed to have properties superior to those of either components taken separately. A similar mixture comprising the ampholytic detergent N dodecyl taurine and of an anionic detergent of the sulphated polyglycol ether type is also reported as superior with regard to foaming to either components (41).

With cotton fabrics Ulman et al (50) found that an increase in water hardness or a decrease in product concentration (from 1.5 g/l to 1.0 g/l) reduced detergency, but the nonionic formulations were much less affected than those based on the anionic formulations. They also found that the 1:1 blend (of nonionic:anionic) retained most of the insensitivity to low concentration of nonionic formulations. Cotton/polyester permanent press, cotton and polyester fabrics soiled with synthetic sebum were studied. They also found that blending of a nonionic and an anionic detergent in a 1:1 ratio resulted in performance close to or even better than that of the nonionic detergent alone.

Gaydos (27) studied the removal of oily soil from three fabrics (rayon, acetate and polyester) using three detergents (an anionic, nonionic and 1:1 anionic:nonionic blend). It was seen from this study that the nonionic detergent removed a greater per cent of oily soil from the rayon and polyester fabrics, while the blend detergent removed a slightly greater per cent of oily soil from the acetate fabric than the other two detergents.

The properties of adsorbed mixed monolayers determines the washing efficiency of mixtures of anionics surfactants with other types of surfactants (cationic, nonionics) of certain conditions are met in such mixtures adsorption and detergency are significantly increased.

2.3 Research studies in soiling and detergency

Soiling may take place in many ways. Fabrics may become soiled in use or even among laundering when soil may be removed from one fabric and deposited on another or redeposited on the same fabric (14).

According to Kissa (34) the most important soiling mechanism is transfer soiling which always involves mechanical work and is accomplished by pressure, abrasion, impingement etc. The main cause of soiling is adhesion of the soil particles to the fiber surface and not mechanical entrapment of soil. The strength of the adhesive bond depends on the forces of interaction per unit interfacial area, the area of contact and whether a liquid is present on the fiber surface.

Soiling can involve methods in which soil is applied directly to the fabric or indirectly from a soiled substrate such as a felt or foam cube. In the direct method the soil may be applied to the fabric with or without pressure. All these methods are designed to simulate actual soiling conditions and are usually followed by a laundering procedure and visual or instrumental measurement of the soiled area of the fabric.

There are two types of soily matters-dry or particulate soil and oily or greasy soil. The former includes particles of dust, sand, earth, soot metallic oxides and carbon with tarry substances may be hydrophillic (metalic oxide) or hydrophobic (carbon) in nature. The latter includes glycerides of long chain of fatty acids and alcohols, lubricating oils etc. which are mostly hydrophobic (57).

In most cases the artificial soil was not to duplicate a natural soil, but rather was to develop a model soil. What is usually desired is not a substance that will faithfully reflect quantitatively the detergent power of the soap, solvent, or process, but rather a substance that will show small differences in detergent power. For all practical purposes, the natural soil in most fabrics can be completely removed by a commercial detergents or a detergent mixtures. It is thus not needed to develop an artificial soil for use as a test model material as replicate of natural soil. The model soil should be so difficult to remove that no detergent or process can completely do so. On the other hand it should be removable to a sufficient degree that significant differences in detergent power can be measured (41).

The artificial soils which have been used in testing fabric detergency vary quite widely in composition and there is a large element of arbitration in their formulation. One of the most important factors in soiling is to make sure that the fabric is in a reproducible standard state before the soil is applied. It is important the fabric is desized and scoured thoroughly, otherwise the artificial soil which is applied will be contaminated by the soil already present in the fabric and the combination will not show standard detergency characteristics. Most of the soils which have been described in the literature in which are furnished by laboratory supply houses, contain carbon together with a mixture of oils, fats or waxes. The different soils may not rate a given group of detergents in the same order and it has been checked so numerous times in different laboratories.

The most variable factor in detergency evaluation is the nature of the dirt. The dirt that accumulates on clothing during daily use is always a mixture. The component of this dirt will vary according to environment, fabric used and personal habits and it is not possible to list all possible dirt types and combination. But this complex mixture can be considered under two general categories, one a more or less fluid component which may be like oil or grease and a solid component made up of small particles and another class of dirt which may be attached to fabric by ionic bonds, or by chemical forces. Many stains fall into this category and require special chemical agents to break the bonds before the stains can be removed (18).

The particulate dirt is generally considered to be more important than the oily component because it is more difficult to remove and it produces the visible effect. Many investigators have used carbon black as particulate dirt. The British Launder's Research Association advocate a mixture of fat and graphite as a artificial soil.

The use of carbon as a representative dirt has, however, some disadvantages. It varies in particle size and in the nature of surface most of the carbons are negatively charged, in aqueous solution. Some are positively charged. Reproducibility of results between different batches of carbon is poor in dilute solution of detergents. Finally carbon bears little relation to natural dirt since if the particle size is very small it may not even differentiate between a good and a bad detergent (18).

According to Harris (30) a test soil comprises of a binding agent and a material which permits quantitative estimation of its removal like a natural soil. Since soot is a common soiling agent and certainly lends itself to reflectance measurements against a white fabric, it is not unusual that carbon in some form should be used.

By several researches (40) it has been reported that a nonionic detergent is effective in removing fatty soils from polyester substrate. Fatsumi and Tsuji (40) found that a nonionic detergent give better detergency than an anionic detergent on polypropylene fabric. Fort et al and Lewis also reported that an anionic detergent is more effective in the removal of fatty soil from a cellulose substrate.

Hunter et al (32) found that built anionics seemed to be as good a detergent as built nonionics at higher concentrations for cleaning of mercerized cotton, mercerized cotton (treated with a flourinated durable water and oil repellent finish) polyester and polyester cotton (65:35) blend fabrics.

Hunter and Ruga (24) found that a change from an all anionic to an all nonionic detergent system showed little or no advantage. A higher active ingredient concentration (2 g/l) was used with the all-anionic system than with the all nonionic system (1.5 g/l). The fabrics included in the study were cotton, polyester cotton (65:35) unfinished, with a durable press, finish and a soil release finish. It is also reported that the detergency of a cellulose substrate was much less affected by the use of a low concentration of an all anionic active built detergent than was the detergency of the polyester substrate.

Fort et al (27) also reported that the rate of removal of fatty soil from polyester film at 20°C increased as nonionic concentration was raised to a maximum near .6 g/l active agent then fell at higher concentrations.

Malak and Chand (17) determined the critical micelle concentration values of the nonionics surfactants by an electri-capillary curve and by spectrophometric methods. They compared the critical micelle concentration value of nonionic surfactants with those of ionic surfactants and found that the former have smaller critical micelle concentration values than the latter. Factors reported were (i) greater hydration of the nonionized polar groups, (ii) greater tendency of nonionic groups to associate because of a lack of electrical charge and (iii) absence of counter ions in nonionic surfactants.

Furry (23) investigated the laundering of white nylons and reported that in soft water, the soaps and built sodium lauryl sulphate were the most efficient detergents. All the detergents studied removed less soil in hard water than in soft water.

Galbraith (24) studied the cleaning efficiency of home laundering detergents. Fabrics were soiled by immersion in a mixture containing colloidal graphite, dispersed in mineral oil, hydrogenated vegetable oil and carbon tetra chloride and were washed with 0.1%, 0.2% and 0.3% concentration at 70°F, 120°F and 140°F by distilled and hard water. It was reported that soaps and built high sudsing soiled synthetic detergents were superior to unbuilt detergents in both soil removal and whiteness retention. Optimum detergent concentrations were 0.2% for soft and 0.3% for hard water (250 ppm). Washing temperature was an important factor in determining the amount of soil removal from all fibres except nylon. On most fibers washing at 120°F or 140°F removed more soil than washing at 100°F which, in turn, removed more soil than washing at 70°F.

Singh and Bhanote (50) conducted a comparative study of cleansing efficiency of synthetic detergents. Samples of white polyester-cotton blend fabric were soiled artificially by padding method and were washed with the selected detergents at different concentrations, temperatures and washing times.
The findings revealed that the optimum conditions for washing with hard water were 2% concentration 50°C temperature and

30 minutes washing time. The cleansing efficiency of the synthetic detergents was found to increase with concentration, temperature and washing time but it was found to decrease in case of washing time when it was increased beyond the optimum value is 30 minutes. Surf was found to have the maximum cleaning efficiency.

Gordon and Shoba, Ulman <u>et al</u> and Lewis (40) reported that the detergency of polyester substrates, soiled with fatty soils, was greater with a nonionic detergent at lower temperatures than at higher temperatures. They also reported that the detergency cellulose substrates soiled with fatty soils using a nonionic detergent was greater at higher temperatures than at lower temperatures. The temperatures used in the study were (Gorden and Shoba) 60° and 120°F, (Ulman <u>et al</u>) 60° and 120°F and (Lewis) 120°, 140° and 160° (27).

The effect of temperature of the wash solution on the removal of oily soil from fabrics has been studied by several investigators. The temperature at which the greater amount of oily soil was removed from the fabrics depends upon the type of fabric and the surfactant used by the investigator.

Spangler <u>et al</u> in studying the reduction in yellowing of cotton, polyester and other fabrics, soiled and washed, they found an improvement in detergency and attributed it to the addition of a nonionic detergent to an anionic detergent.

The greatest benefit on cellulose was in warm conditions (120°F). This was reversed with polyester where detergency was better at the lower temperature 60°F.

The anionic detergent removed a much greater per cent of Nujol mineral oil from polyester fabric than from rayon or acetate fabric. This finding is partially in agreement with that of Lewis (40) who found after one laundering that a greater percentage of oily soil was removed from polyester fabric.

Bowers and Chantrey, Fort _et al_, Gorden _et al_, Ulman _et al_ using equal concentration of the active ingredient reported that nonionic detergent was more effective than anionic detergents in removing oily soil from fabrics (11, 27).

On the other hand several researchers have also reported that an anionic detergent was more effective than a nonionic detergent in removing oily soil from cellulose fabric (27).

Furry (22) and his collaborators examined numerous preparations made from soaps and from synthetic detergents, with and without builders. Soap is more effective in removing soil from cotton. Alkyl sulphate are not as good as soap showing in fact only 75-85% effectiveness. Parkhurt has stated that so far synthetic detergents have not equalled soap in this field except in hard water but the margin between the two classes of products is rapidly narrowing. Soaps are only effective in neutral alkaline bath. They cannot under any circumstances be employed in acid bath.

For cotton soaps are considered as better detergents than sulphates and sulphonate detergents as soaps (when used in water with no Ca and Mg salts, builders of other solutes) show higher soil suspending power than sulphated and sulphonated detergents (58).

In a study of the soil removal and soil redeposition tendency of different fabrics by Bansal, the following results were reported. When the washing period was long (45 mins) equilibrium was established between desoiling and wet soiling tendency of different fabrics. Presence of another fiber did not have much influence on soil removal. Very high redeposition of soil took place on nylon and terylene followed by rayon and minimum redeposition of soil took place on cotton fabrics. When washing period was short (10 mins), soil redeposition took place only on nylon and terylene while that on other fabrics was nil or negligible. Thus effective cleansing depends upon the soil suspending power of the cleansing solution. For effective cleansing, concentration above 2 g/1 of soap was found to be necessary.

In a study by Furry and McLendan (22), the synthetic detergent in different concentrations removed less soil from cotton fabric as compared to soap. For most anionic and nonionic detergents, the washing efficiency was greater at 1.5 g/l than at 0.5 g/l concentration. The efficiency increased upto 2.5 g/l per cent and then remained constant. The cationic detergent were inefficient in removing soil at the different concentrations.

The major findings in a study on soiling and cleaning by Chaudhary (12) were: Maximum soil was removed from all the samples in case of both (long cloth and poplin) fabrics at 5 g/l concentration of commercial soap (501 bar soap) and commercial synthetic detergents (Det and Teepol). When a comparative evaluation of the three cleansing agents was made, it was found that the commercial soap ranked the highest in removal of soil from both the fabrics as compared to the commercial synthetic detergents. The two fabrics showed differences in their soiling as well as washing, although the conditions of soiling as well as washing were the same.

Terry (54) compared solvent soiling and emulsion soiling of different fabrics and their cleansing with soap and synthetic detergent.

The results of the study were as follows:

More soil was removed from samples soiled with emulsion technique than with the solvent technique. Commercial soap (501 bar soap) indicated that, it has better cleansing efficiency than the synthetic detergent (Teepol). More soil was removed by the commercial soap (501 bar soap) at higher concentration than at lower concentration, but with the synthetic detergent (Teepol) concentration did not have much effect.

The wetting time of soiled fabrics differed with solvent and emulsion techniques. The wettability of emulsion soiled samples was slightly higher than the solvent soiled samples for cotton while the reverse was the case with polyester and silk samples. The wetting time of different samples cotton, silk and polyester after washing with two concentrations of washing agents was different, the wetting time being higher for samples washed at lower concentration. It was explained as due to the redeposition of the soil on fabric at lower concentration and the wetting time increased.

Sharma (49) studied the soil removal efficiency of different cleansing agents at different concentrations. Soiled samples of cotton, wool and cotswool were used. Laundering of the soiled samples was carried out in the Launder-Ometer. The major findings of the study were that the maximum soil was removed from cotton fabrics with 501 soap solution at 5 g/l concentration and the least by Teepol at all concentration. Teepol gave better results on wool. Sodium lauryl sulphate gave good results in cotton, wool and cotswool and there was no staining. Better results were found by combining soap and sodium lauryl sulphate than with the combination of soap and Teepol. When a comparative evaluation of these cleaning agents were made it was found that Teepol removed the least amount of soil from soiled cotton.

In an earlier study done by the author, Cheema (13), five different soaps and synthetic detergents were studied for their washing efficiency on soiled cotton fabric. Washing of cotton poplin test fabric was carried out at room temperature at four wash timing : 5, 10, 20 and 30 mins. It was seen from the study that the maximum cleaning took place in the first 5 to 10 mins. The efficiency for soil removal of the agents used was in the decreasing order of cleansing ability - 5 g/l of 501 soap, 5 g/l of a mixture of Lux and sodium lauryl sulphate (2.5 g/l of each), 5 g/l of sodium lauryl sulphate, 5 g/l of a mixture of Lux and Teepol (2.5 g/l each), 5 g/l Lux alone and last 5 g/l Teepol and 5 g/l of Lissapol D.

2.4 Recent trends in washing machines

In a study by Feldtman (21) three different commercially available washing machines were used. The details of which are given below :

Washing Machine No.	Mechanical Action	Machine Speed
1	Agitator	40 cycles/min
2	Rotating drum	60 rev/min
3	Impeller	710 rev/min

Mechanical action during washing was compared by comparing the retention of set in polymer treated wool, it was seen from the results that the low speed agitator type had a mild action and caused the least loss of set whereas the machine with the impeller action severely distorted the samples and caused the greatest loss of set as the impeller type action has whirling action and may have caused partial twisting and flexing of the fabric. The machine with the rotating drum action have a comprehensive action and gave intermediate results. But where fitting is concerned rotating drum type is more severe than the impeller type machine. The severe impact loss comparison sustained by the samples in the rotating drum machine are apparently very condusive to felting.

In a study by the author (13) on the fabrication and the study of the performance of a small washing machine, the machine fabricated in wood and aluminium parts worked on the principle of stirring mechanism from above in a bucket and this reduced the cost of the container and cost of casing and facilitated to have a bucket load of washing, since the agitator was in a bucket. Tests were carried out to assess the performance of the washing machine. Samples were soiled by the emulsion method. The following were the variables :

(a) by varying time of washing (5, 10, 20 and 30 mins),

(b) by varying cleansing agents (501 soap, Lux soap, Teepol , sodium lauryl sulphate and two combinations of Lux plus Teepol and Lux plus sodium lauryl sulphate, (c) stirring intensity, (d) different shapes of stirrers.

The cleansing agents were compared for their efficiency of soil removal with stirring in a Launder-Ometer and the experimental washing machine. It was seen that it was similar and equivalent. A separate pretreatment was recommended for the removal of stains. The shape of the stirrer under the conditions used, did not have any variations in cleaning performance of samples.

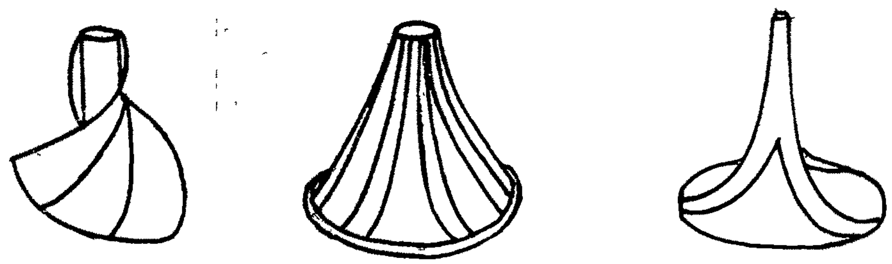
The washing machine so fabricated with an overhead stirrer was quite good for the load half lb studied. Further work on fabrication of a washing machine for a higher load (one lb or more) and with more durable mechanisms (in metal based on above research work of the author) was thus necessary.

Types of washing machines: According to Manmade Textile Encyclopedia (44) edited by Press, commonly there are two types of washers : (a) conventional type and (b) automatic type.

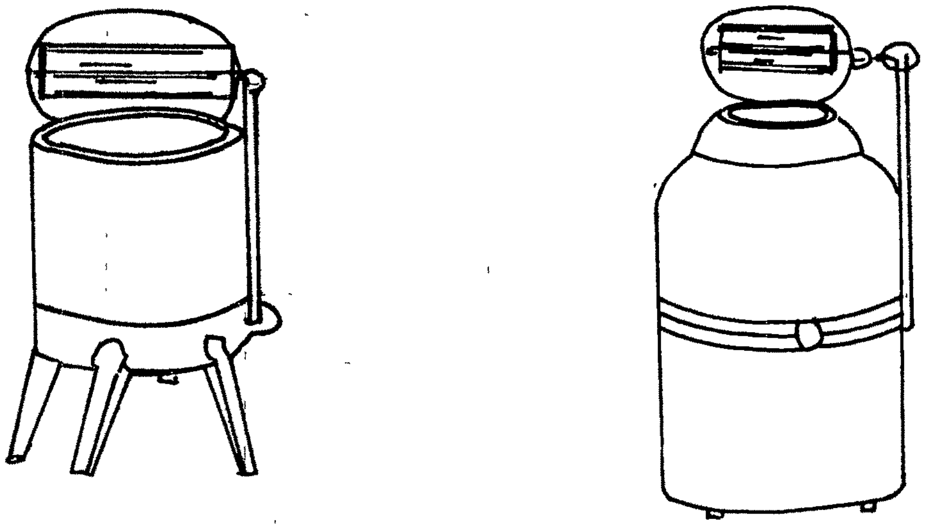
(a) Conventional type : In the conventional type machines the agitator is attached to an oscillating shaft in the centre of the tub (Fig 7a) as it turns back and forth the clothes are twisted through the water. These have either a wringer or a spinner basket for extracting water after the clothes have been washed. In the wringer type the water is extracted by putting

FIG. 7

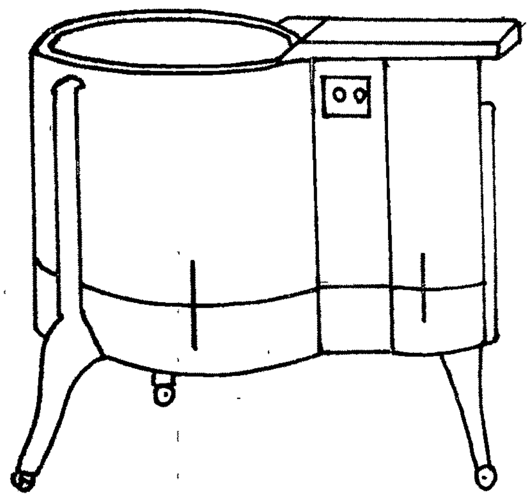
CONVENTIONAL TYPE



(a) OSCILLATING SHAFT



(b) WRINGER TYPE



(c) SPINNER TYPE

the clothes through a set of rubber rollers called wringers (Fig 7b). In a spinner type, clothes are transferred to a second smaller tub and water is spun out by centrifugal force (Fig 7c). In a conventional washing machine, the full washing cycle that is washing, rinsing, squeezing and drying is not a continuous process, as in an automatic washer.(Fig 8).

(b) Automatic type : Automatic type washer can be defined as a machine which when set into operation by the user, automatically fills the tub with the required amount of water, heats the water at the temperature selected after adding the detergent mixing, washes for a pre-set time, rinses and extracts water and shuts itself off without any further attention.

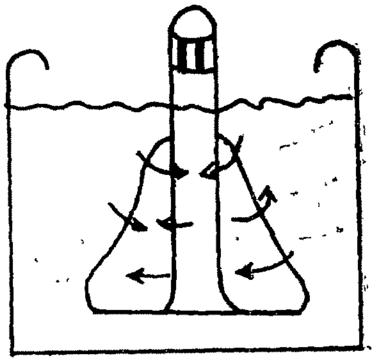
Automatic washers have the following washing principles:

i) Oscillating agitator : An agitator mechanism equipped with blades or fins which oscillates back and forth in a central part and agitates the load (Fig 8a).

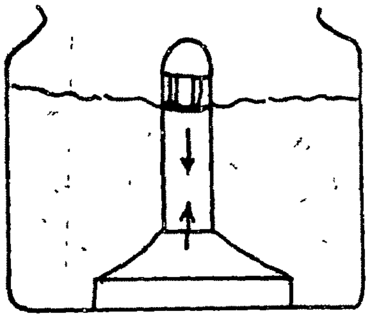
ii) Pulsator agitator : An agitator with rubber fins at the top and skirted bottom, operates in an up and down motion. This action circulates amount of water from the top to the bottom of the tub forcing it repeatedly through the clothes as they are kept moving. The cleaning action depends mainly on the water movement (Fig 8b).

iii) Cylinder or tumbler type : A perforated cylindrical tub having edges or projections on the inside revolves on either a

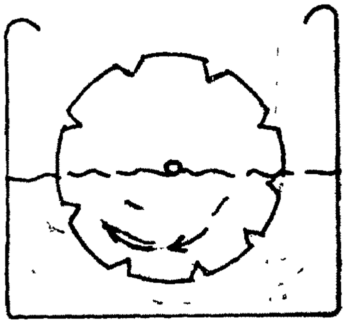
FIG. 8
AUTOMATIC WASHERS



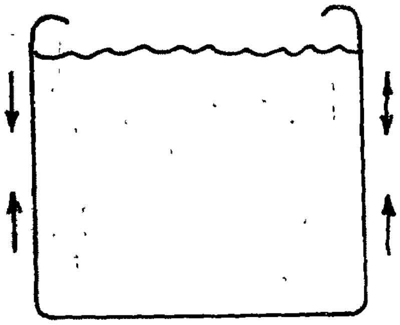
(a) OSCILLATING AGITATOR



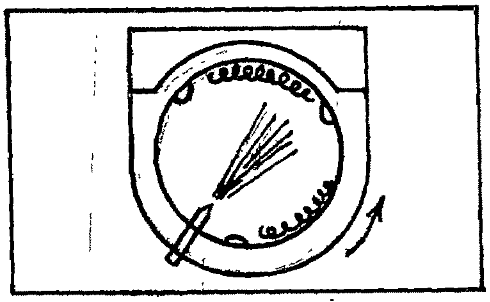
(b) PULSATOR AGITATOR



(c) CYLINDRICAL TUMBLER TYPE



(d) AGITATED TUB



(e) CYLINDRICAL HORIZONTAL SPRAY

horizontal or inclined axis within an outer tub which contains the wash water and as the cylinder revolves the clothes are raised on the edge of smooth rounded projection and then dropped into the water thus creating a cleansing action (Fig 8c).

iv) Agitated tub : A bouncing or tossing of the inner tub creates a motion of the water in an up and down direction in a manner similar to a hand shaken. This action sets the clothes in motion against the interior side of the tub which have swirled ridges and forces the water through the clothes (Fig 8d).

v) Cylindrical horizontal spray : The load is lifted by a baffle through the saturating spray of washing solution then dropped to the bottom of the cylinder. The dirty solution released by impact drains to the reservoir below the cylinder for heating and filtration (Fig 8e).

The automatic washers have some features in common regardless of the types. Many of these features have been especially designed to care for modern fabrics made from both natural and manmade fibers. Styling of these features changes from year to year with equipment and fabric developments but the features themselves or principles themselves are unchanged functionally.

Among the mechanical devices which are used, the Launder-Ometer and Tergotameter represent small versions of a tumble type and an agitator type washers. It is difficult to duplicate the mechanical effect of a full size washer with a small counterpart but the machines are self-consistent and can be correlated with others (47).

<u>The types of washing machines and their specifications</u>

ISI standards on domestic commercial washing machines described the related terms as follows :

Domestic electric washing machine - An electrical appliance designed principally for the washing of household linen, which incorporates means for agitating and which may incorporate means for subsequently extracting water out of the wash load.

Non-automatic/Semi-automatic washing machine - Washing machines in which the successive operations of the complete system requires one or several interventions from the operator.

Agitator - A part for agitating the washing solution in the tub by rotation or by reciprocation.

Related capacity of the water washing unit - The maximum mass of dry textiles handled by the washing unit at a time, preferred rated capacity being 1.5 kg, 3 kg and 6 kg of dry textile material.

Specification of some washing machines

The features of washing machines have been summarised by manmade textile encyclopedia (38) and are given below.

Washing time	Regular (max)	10 - 20 mins
	Short	75 - 4 mins
Total cycles	Regular (max)	26 - 45 mins
	Short	12 - 25 mins
Number of deep rinses	1 or 2	
Speed of wash and rinse action (rpm)	Regular	30 - 70
	Special	21 - 37
Spinning speed (rpm)	Regular	500 - 1140
	Special	412
Hot water used (gal) (approx)	Full load	6 - 24
	Small load	6 - 10
Total water used(gal) (approx)	Full load	26 - 42
	Small load	14 - 29
Total capacity dry clothes	8 - 10 lbs	
Tub capacity	7 - 17 gals of water	

Table 4 Names of commercial washing machines using impeller for mechanical action

Specification	Brooks	Dukes	Arvind (Delux)	Niki Tasha	Dewaan	Bajaj	Elite	Maharaja	Clean Wash	Radhika
<u>General Specification</u>										
Load dry weight (kg)	3	3	4	3	2.75	3	3.5	3	1.8	1.5
Container	Stainless steel	Aluminium	Aluminium	Vitereous enamel	Aluminium	Anodized aluminium sheet	Galvanized sheet	Fibre glass	Aluminium	Aluminium
Cost (Rs.)	7900	3800	2695	6175	1985	3725	3100	3000	2550	1250
Weight of the machine (kg)	45	25	31	64	26	26	-	25	-	8-10
<u>Mechanical Specification</u>										
Motor capacity (HP)	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/3
Motor (RPM)	300	300	1400	1440	1495	1440	1440	1440	1440	1440
Auto/Semi-Auto	Semi	Semi	Semi	Auto	Semi	Semi	Semi	Semi	Semi	Semi
<u>Washing Specification</u>										
Time for washing (mts)	3	2-3	4-7	-	-	4	-	-	3	10
Amount of water required (lit)	-	-	40	-	50	14	40	-	12	5-7

Table 4 contd..

Impeller for Mechanical Action

Specification	Anand	Elegant Racold	Mini-Arvind	Nirmal Uniwash	Dhawal Uniwash	Krishna	Ambica	Natraj
<u>General Specification</u>								
Load dry weight (kg)	2	2	2	2.75	2.75	$1\frac{1}{2}$-3	2.3	1.5
Container	Aluminium	Aluminium	Aluminium	-	-	Aluminium	Aluminium	Fibre glass
Cost (Rs.)	1600	3800	1980	4800	2950	1550 -4550	2300	5450
Weight of the machine (kg)	-	-	20	50	28.5	15-42	13	4
<u>Mechanical Specification</u>								
Motor capacity (HP)	1/4	1/6	1/8	1/3	1/4	1/4	1/4	1/4
Motor (RPM)	1400	-	1400	1200	1200	1440	1440	1440
Auto/Semi-Auto	Semi	Semi	Semi	Semi	Semi	Semi	Semi	Semi
<u>Washing Specification</u>								
Time for washing (mts)	4	-	4-7	2	4	3	-	15
Amount of water required (lit)	-	-	20	-	-	5-10	-	-

Most commercial washing machines are using an impeller and provide agitation for the cleaning of clothes. An impeller give the movement of the wash solution.

From the above table one can conclude that almost all -

(a) machines are semi-automatic
(b) capacity varies between 1.5 kg to 4 kg dry weight usually between 2 to 3 kgs
(c) time for washing varies between 3 to 7 minutes
(d) there is a lot of variation in the cost which mainly depends upon the type of container and capacity
(d) motor capacity is usually 1/4 H.P. and RPM 1400.

Table 4 contd..

Specification	Savior	Racold	Novella	Americ
	Tumble Wash Principle			Oscillating Agitator
General Specification				
Load dry weight (kg)	3.75	5	2	3
Container	Stainless steel	Stainless steel	Plastic	Fibre top and aluminium galvanized body
Cost (Rs.)	8900	6100	6000	3125
Weight of the machine (kg)	100	-	10	-
Mechanical Specification				
Motor capacity (HP)	72 W	-	100 Watts	1/3 HP
Motor (RPM)	550	-	-	60 strokes/minute
Auto/Semi-Auto	Auto	Auto	Semi	Semi
Washing Specification				
Time for washing (mts)	Total 45	-	-	10
Amount of water required (lit)	55	100	10-12	10
	Tumble wash or the rotary drum principle to provide mechanical action to the clothes are also available. But not many manufacturers are there. This principle provides agitation to the clothes. There are both small capacity and large capacity ranging from 2 kg to 5 kg dry wt. The main drawback being that the cost of these machines is high.			In these washing machines the central shaft oscillates and gives agitation to both the solution and the clothes. Only one machine using this principle was available in the market.