STUDIES ON THE EMULSION SCOURING OF RAW WOOL

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by

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C O N T E N T S

1. AIM AND SCOPE OF THE PRESENT STUDY.

Knowledge of the mechanism of detergency under various conditions has thus far been built up from laboratory studies. It is well known that the laboratory methods for determing detergency are on the whole not able to give results which agree with those obtained in practice, probably because the actual scouring conditions cannot be duplicated exactly in the laboratory.

Detergency testing on a full industrial scale is virtually impossible in view of the high cost and the production losses involved. In commercial raw wool scouring, which is an extremely complex system, it would be very difficult to exercise proper and complete control. The study described here was carried out on a specially constructed pilot plant which is similar to a full-scale plant in that the lengths of the bowls are of the same order as those of industrial plants, but they are considerably narrower. The trials were carried out under strictly controlled conditions in which the effects to be studied were created by the necessary changes while all other factors were kept constant.

The pilot plant experiments were planned from indications of laboratory studies and the results were expected to be more comparable with those obtained in industrial practice.

The effect of several factors on the scouring of raw wool was studied from the detergent efficiency aspect. The factors investigated were: mechanical action, backflow, temperature and detergency builders. A number of detergents which were selected from the large range which is available were compared with regard to efficiency and economy of scouring.

A difficulty which hinders quantitative laboratory work on nonionic detergents is the fact that there is no rapid, accurate method for the estimation of nonionic detergents. The analytical methods which are employed at present are interfered with by virtually all the impurities which are normally present in scouring liquors. Some of the existing methods have been investigated and tested for precision and reproducibility and an attempt was made at establishing a new method.

The sorption of nonionic detergents by various substrates has not been fully investigated because of the above reason and also because the amounts of detergent sorbed by most substrates are very small and difficult to determine. Attempts were made at determining the sorption of nonionic detergents onto wool and impurities which are normally found in scouring liquors. A new method for the investigation of "inactivation" of detergent by contaminants present in scouring liquors, which may be regarded as an indirect indication of detergent sorption, was investigated.

SECTION I : PILOT PLANT STUDY.

2. INTRODUCTION.

2.1 General.

The impurities which have to be removed from raw wool during scouring are complex. Different types of raw wool from different sources differ widely in the amount and type of contaminants they contain. The main impurities present in raw wool are

a) Sand and dust,
b) Vegetable matter,
c) Faecal matter,
d) Suint, i.e. dried sweat,
e) Wool grease.

The particles of sand which are not held by the grease on the fibres are removed simply by dropping off onto the bottom of the scouring bowls. The vegetable and faecal matter is not normally removed during scouring.

Suint contains variable quantities of potassium salts of higher molecular weight fatty acids[1], i.e. potassium soaps. These soaps and other inorganic salts present are desirable constituents, in that they assist in the scouring process by improving wetting of the wool and by subsequent emulsification of wool grease. The wool grease present on the fibres is mainly responsible for the consumption of detergent. Cholesterol and its associated isomeric compounds, which are the main constituents of wool grease[2], are unsaponifiable.

Raw wool may yield as little as 20% clean wool on scouring. The result is that the scouring liquors rapidly become loaded with grease, suint and dirt, which makes the physico-chemical investigation of the scouring liquors a highly complex problem.

The treatment of scouring effluents has become a factor of growing importance with the advent of water pollution control[3] and is the subject of a vast body of literature[4-6].

2.2 Systems of scouring.

Each of the numerous commercial scouring methods is claimed to have advantages over the others from the point of view of some of the following aspects: economy, mild chemical action on the fibres resulting in little damage, whiter colour, ease of operation, degree of entanglement of the fibres, etc. All these properties are important if it is kept in mind that scouring is the first step in processing raw wool and that the treatment received by the wool in scouring will be largely responsible for its behaviour in subsequent processing[7]. Williams[8] has found from laboratory trials that there is a measurable difference in yield when wool is scoured in different ways. The differences are ascribed to the dissolution of oxidised protein material from the tip portions of the wool fibres by hot alkaline scouring solutions.

a) Emulsion Scouring.

This is the oldest known method of scouring. With the advent of synthetic detergents of all types this process has undergone a number of changes from the original soap-soda scour.

i) Soap and soda scouring.

This method of scouring is still employed in industry, especially in Bradford where the authorities have decreed that synthetic detergents should not be used for wool scouring, supposedly in order to facilitate grease recovery from the effluent.

In its classical form, this process entails scouring raw wool at temperatures of not less than 45°C, which is the average

melting point of wool grease[9], in a scouring set of four or five bowls, of which the first two or three (depending on whether or not grease recovery is practiced) contain soap and soda ash, usually only sufficient to keep the pH in the first bowl (or second) in the vicinity of 9.0 to 10.0. Originally it was thought that the soda ash assisted the scouring process by saponifying the wool grease, but it has since been shown that the maximum proportion of saponifiable matter in wool grease is in the vicinity of 0.5%[10]. There is therefore no justification from this point of view for the addition of large amounts of soda ash, since too high a pH leads to the degradation of wool fibres, causing them to lose some of their desirable physical properties, and also causes trouble in dyeing.

ii) Nonionic detergents.

Nonionic detergents are a fairly recent replacement for the traditional soap scouring methods. This system gained fairly slow acceptance at first, partly due to the fact that the recommended temperature of use was in the region of 70°C[10] which gave rise to rather unpleasant working conditions. It was subsequently found that nonionic detergents, when used in a counterflowing system at 60° to 63°C gave a scour equal or superior to the one obtained with soap and soda. In some mills the nonionic detergent is used in conjunction with soda ash or neutral builders such as sodium chloride and sodium sulphate[11,12].

It is claimed that wools scoured under neutral conditions using nonionic detergents are softer, whiter and have a loftier handle[13]. A further advantage lies in the fact that

the nonionic detergents are insensitive to hard water and that, unlike soap, they are not adsorbed by wool to any great extent and give no trouble in rinsing and subsequent wet processing. Nonionic detergents also give a reasonably good grease removal under acid conditions[3].

(iii) Iso-electric scouring.

Wool, which is an amphoteric oompound, is neutral at its iso-electric point which is in the vicinity of 4.5[10]. There was an attempt[14] during the Second World War to scour wool at this pH in acid medium, since it was anticipated that the chemical degradation of wool would be reduced to a minimum and that the best possible physical properties and appearance would be produced under these conditions.

This process suffers from the disadvantage that only nonionic detergents remain efficient at these low pH values and that corrosion of the scouring equipment then becomes excessive.

b) Solvent Scouring.

The solvent scouring process is one in which the wool grease is removed by an organic solvent other than water, normally followed by an aqueous rinse to remove suint. Almost every possible fat solvent has been suggested and all of them would probably be satisfactory if grease removal were the only requirement. Solvents are, however, also judged on cost, availability and fire-hazard[15].

The first solvent scouring process was tried in the 1880's[16,17] using acetone and ether as solvents, but was immediately abandoned because of explosion and fire hazard.

Some years later, carbon bisulphide was used as a solvent, but was abandoned since it was absorbed by the wool, rendering it permanently yellow, and because of its unpleasant odour and fire hazard.

Some of the other solvents which were examined took the extraction too far: the grease should be removed from the surface of the fibre only[18], since if grease is removed from the cortex of the fibres, the scoured product becomes very harsh and brittle[19].

A moderately low-boiling aliphatic hydrocarbon has been employed successfully for many years by a large American industrial concern. In this process, the wool has to be given an aqueous rinse to remove suint etc. Chlorinated hydrocarbons (mainly trichloroethylene) have been used in the Smith-Drum process.

Experiments have been carried out on the use of a mixture of methanol and ethanol as a solvent because of its alleged effectiveness in removing suint as well as grease, but it was abandoned because of economic considerations. It has also been pointed out that the addition of butyl alcohol to the conventional emulsion scouring system has advantages as far as effluent purification is concerned[20].

The most successful attempt at overcoming the problem of dissolving the water-soluble impurities in a solvent scouring system seems to have been the Australian process[21] where the wool is carried on a lattice and is jetted with white spirit under pressure to remove wax and dirt and then with water to remove suint, etc. It is claimed that far less felting takes place than with aqueous scouring and that the combing yield is increased considerably. This process is now in industrial use.

c) Other systems.

Anderson and Poulter[22] have recently described a method similar to the above Australian solvent scour. Similar equipment is used, but the solvent is replaced by a solution of a nonionic detergent with an alkaline builder. Satisfactory scouring was obtained and it is said that a minimum of felting takes place and that the expensive solvent recovery process is eliminated. This process is under development.

An interesting process has been developed at the University of New South Wales, called "aqueous compression jet scouring"[23,24] in which raw wool is fed into the scouring set on a porous tensioned conveyor belt. The wool is compressed between a rotating porous drum and the conveyor belt and jetted with aqueous scouring liquor from both sides to remove wax, suint and other extraneous matter. The wool is then squeezed and transferred to a lattice conveyor. This process yields a uniformly scoured product which has undergone very little felting, resulting in small loss in mechanical processing and higher comb yield. The process is under development.

Another method of scouring which is still in use is the Duhamel suint process. Here the suint salts are dissolved in the first bowl at a relatively low temperature. This liquor is then pumped to the second bowl where it is used as a scouring assistant together with a detergent. Scouring with suint liquors[25] without additional detergent or alkali is a relatively mild treatment and does not damage the fibres unduly. It has been found difficult in some cases to reduce the grease content to a sufficiently low level when no additional detergent is used.

A novel cleaning process, the "Frosted Wool process", was introduced in 1935[26] but it did not survive World War II. The wools were subjected to temperatures of -30° to -50°F to freeze the grease which became very brittle. Subsequent opening and dusting shattered the frozen grease to a powder, and a considerable proportion was thus removed from the fibres. The cleaned wool obtained was delivered in a dry, open and lofty state, but subsequent scouring was necessary to remove the excessive residual grease, suint and dirt still remaining on the wool.

2.3 Factors affecting detergent efficiency.

It may be concluded from the literature that there are several factors in scouring which are known to affect detergent efficiency in one way or another. The mechanism by which the changes influence detergency is not always known, but sufficient work has been done in order to establish the fact that the influences are significant and measurable.

An increase in mechanical action has been shown to have a beneficial effect on detergency[27,28,29]. In raw wool scouring the problem is more complex, in that cleanliness of the scoured product is not the only object; the wool is to be delivered in as open as possible a form for further mechanical processing. Since excessive mechanical action could cause more felting, a compromise has to be found between decrease of detergent consumption and structure of scoured wool.

The temperatures of the scouring liquors have to be above the melting point of the wool grease which normally lies in the range 40° to 50°C[9,28]. The temperature of the scouring bowls affects detergent consumption[22,28]. In the case of nonionic

detergents, it was found that once a certain temperature has been exceeded, the increase in detergent efficiency is less marked. In the view of Lawrence[30] the large temperature coefficient of detergent processes is a result of the increased rate of diffusion of detergent into the dirt at higher temperatures.

It has long been known that limited addition of neutral electrolytes causes an increase in detergent efficiency[31]. For ionic detergents it was found that only the ions with charges opposite to that of the detergent ion had an effect, and it was shown that high salt concentrations caused a decrease in detergency. Several workers have pointed out the increase in capillary activity of detergents in the presence of electrolytes[32,33]. The same general observations were made by McLaren[34] who studied nonionic detergents in the presence of salt and found an initial increase in detergency followed by a subsequent decrease as the salt concentration is increased. pH has also been shown to have an effect on dirt removal, although the conclusions are not as clear-cut since they depend on the type of detergent used, type of dirt and the substrate.

In raw wool scouring, the aim of the scourer is to produce a scoured product which is as white as possible. It is known that under certain circumstances, redeposition of soil onto the wool being scoured may occur, e.g. when there is a high concentration of dirt present in the scouring liquors. The presence of suspended dirt in the scouring liquors will have a detrimental effect on detergent consumption since it may be assumed that some of the detergent will be "inactivated" by the suspended dirt, e.g. by adsorption, suspension, etc. The counterflow[35] or backflow system

which is considered to be essential[10] in order to preserve the controllability and economics of a nonionic detergent scour would have the effect of reducing the solids concentration in all the bowls.

2.4 Theories of Detergency.

In view of the extreme complexity of most scouring processes, it would be desirable to divide detergency into a number of separate phases and study the efficiency of the detergent in each phase. Thus the detergent performs at least three functions[27]:

a) Allows the water to wet both the soil and the surface to be cleaned,

b) Is adsorbed onto the surface, preferentially wetting it so that the soil is displaced,

c) Emulsifies oily soil and peptises solid soil, keeping them dispersed so that they can be carried away in the overflow.

If these were the only factors involved in the detergent process and it were possible to measure each separately and if the data could then be combined into suitable mathematical formulae, one might arrive at a detergency rating for a particular detergent from which its efficiency may be predicted. Unfortunately detergency is such a complicated and varied process with so many possible interactions between the various solids, the surfaces, water, detergent and various builders that it is difficult to establish exactly what role the detergent plays. The danger in this type of approach lies in the fact that when a specially constructed, simple system is used[36], the results do not agree with those obtained in practice. This has recently been pointed out by Radder and de Vlieger[37] who showed that no satisfactory methods were available for detergency testing and that, at best, the present methods could only distinguish between a good and an indifferent detergent. The issue is further complicated by the fact that a

detergent may be excellent in one application and a failure in another. Of the present methods, probably the most widely used is the application of pigmented dirt to a clean swatch of cloth[38]. The cloth is then washed under standard conditions and its reflectance measured against a disc of standard whiteness. Again, the results obtained are not comparable with those from actual practice.

For raw wool scouring, the field of detergents may be narrowed down to anionic and nonionic types since the cationic detergents are precipitated when mixed with anionic soaps[39]. Spring[40] suggested that detergent action depends on the alteration of the hydrophobic surface of the solid being dispersed. The same observation was made later from a different approach[41]. The removal of paraffin and olive oil was found to be associated with the matching of the polarities of the oil and fibre. It was shown[42] that oil was difficult to remove from undamaged wool because the fibre has an epicuticle which is mainly paraffinic in nature. When the scale structure is destroyed to expose the underlying hydrophilic keratin, oil removal becomes considerably easier[42].

Studies of detergent action under a microscope[39] show that the essential process is a displacement of the oil from the fibre in large drops. This work was extended by Harker[43] and by Stevenson[44] to include particulate dirt which was found to be removed in a similar way; the oil-dirt globules and the detergent form complexes which are swollen by the scouring liquors and these swollen complexes are removed by the action of the water flowing past the fibres. If there is sufficient detergent present in the system, agitation (water flow) is not necessary since the grease droplets and dirt-grease complexes are then completely dispersed. In a review of the above work, Stevenson[45] describes the mechanism

of oil removal from fibres in terms of solubilization, complex formation and penetration, coupled with secondary effects such as spontaneous emulsification and osmotic swelling.

The theory of Lawrence[30,46] was developed from the observation of the detergence of polar dirt subsequent to a study of the ternary phase diagrams of soap-water-amphiphile systems. The detergence of polar dirt was found to be a spontaneous process of penetration of soap and water into the dirt, followed by peptisation. This process is independent of surface forces and results from cryoscopic forces and diffusion processes in the ternary soap-water-polar dirt system. The minimum temperature of penetration of a homologous series of fatty acids by a variety of detergents is sharply defined and was found to be several degrees below the melting point of the acid. It was concluded that detergency in such systems consists of the initial formation, as a result of surface forces, of a close-packed adsorbed monolayer of soap at the solution-dirt interface, followed by the penetration of soap and water into the dirt and the formation of the various dirt-water-soap phases, which can be removed by agitation, e.g. the flow of liquor past the substrate. The large temperature coefficient of detergent processes may be explained in terms of this theory since the rate of diffusion of detergent into the dirt increases with temperature.

It will be seen that the picture remains somewhat clouded in that, of all the properties which influence detergence, e.g. surface or interfacial tensions, adhesion of the aqueous detergent solution to the fibre, etc., none are fundamental in the sense that it alone is the predominating factor, and a combination or correlation of all these factors may yet prove to be such a

fundamental quantity.

There is some hope that newer techniques such as radioactive tracer methods, when applied to the problem of detergency[47], may throw further light on the fundamentals of the process. These methods have enabled workers to study the removal of each of several oil constituents of soiled clothing separately[48]. Indications have been found that there is a relation between adsorption of a detergent and detergency[49,50], and this type of study could probably be carried out with more prospects of success when radiotracer techniques are used, provided that reproducible and sensitive laboratory washing testscould be devised which agreed with results found in practice.

3. THE EFFECT OF MECHANICAL ACTION ON THE SCOURING OF RAW WOOL.

3.1 Introduction.

It is a commonly held view that agitation in the scouring bowls during the washing of raw wool, such as is imparted by a fast rake speed, will cause an increase in detergent efficiency, but may be accompanied by more felting than mild agitation caused by a slower rake speed[9]. Further, the main part of the cleaning action during scouring is believed to take place at the squeeze rollers where the relative velocity of wool to liquor is highest[28,29]. Another factor which could influence the scouring efficiency is the rate of feeding of raw wool into the scouring set.

In order to investigate the effect of these three factors on scouring efficiency, a series of experiments was undertaken in which uniform lots of raw wool were scoured to a constant residual grease value. The lots were scoured using varying combinations of rake speed, roller speed and rate of feeding. The results of the different scours were then compared by evaluating the consumption of detergent, by visual appraisal of the scoured product and by the performance of the different lots during subsequent processing.

3.2. Experimental.

The study was carried out using a Petrie and McNaught pilot-scale scouring plant. The bowls are of normal length, i.e. first and second bowls 15 feet, third and fourth bowls 10 feet long. The bowls are, however, only one foot wide and have the following capacities:

first and second bowls: 170 gallons each.
third and fourth bowls: 100 gallons each.

These figures include the liquor in the small bowls below the squeeze rollers. The dryer is of the perforated drum type (Fleissner).

The detergent used in the first three bowls was Lissapol NX (I.C.I.), a nonionic synthetic detergent of the alkylphenol-ethylene oxide condensate type[12]. Sodium sulphate (Glauber's salt) was used as a builder in the second bowl and sodium carbonate (soda ash) was added to the first bowl. All percentages are calculated on weights as received.

The different scours were performed on individual lots drawn from a consignment of grease wool (Cape 64's, 8/10 months). To ensure uniformity of the lots, all the wool was blended and passed through a fleecebreaker, after which it was again carefully blended. Each experimental lot consisted of 400 lb. grease wool, which was found to give a sufficiently long running time in the scouring plant to ensure reproducible results. The wool used had a clean yield of 50.8% (calculated on the basis of dry greasy and dry scoured weights).

Apart from the variations in mechanical conditions, all lots were subjected to identical treatments. The bowls were dropped and cleaned out after each lot had been scoured and the rate of back-flow from the rinse bowl to the first bowl was kept constant during the scour at 25 gallons per hour. The temperatures of the bowls were kept constant by leaking steam into them and the initial charges of detergent and builders were the same for all lots (values are given in Table I).

TABLE I

Temperatures and initial concentrations of scouring aids

Bowl No.	Temp. (°C)	Lissapol NX (% w/w)	Soda Ash (% w/w)	Glauber's Salt (% w/w)
1	52	0.006	0,18	-
2	55	0.02	-	0,35
3	50	0,011	-	-
4	40	-	-	-
Dryer	65			

The rate of feed of grease wool was varied in four steps, viz. 100, 133, 166 and 200 lb./hr. The rollers (15 inches wide) were set at 3 tons total pressure and four roller speeds were used, viz. 2,4,6 and 9 r.p.m.; the circumferential speed at the fastest rate is 14.5 cm./sec. Four different rake speeds were also used, the minimum being 5 strokes per minute (s.p.m.), the maximum 14 s.p.m. and two intermediate speeds of 8 and 11 s.p.m. A total of 64 individual lots of wool were scoured in order to cover all the possible permutations arising from four different settings of three variable factors.

The effect of the different rake speeds on the motion of the wool through the bowls is given in Table 2. It will be seen that the total time of immersion of wool in the four bowls is not exactly inversely proportional to the speed of the rakes through the liquor as might at first be expected. This is because several other factors influence the speed of movement of the wool through the train, e.g. the rate of recirculation of water from the squeeze bowls and the amount of turbulence caused by the rakes at different speeds.

TABLE 2

Effect of rake speed on movement of wool

Rake Speed s.p.m.	Total time of immersion in all four bowls.	Speed of main rakes through liquor.
5	5 min. 50 seconds	1.4 cm/sec.
8	4 min. 25 seconds	2.3 cm/sec.
11	3 min. 20 seconds	3.1 cm/sec.
14	2 min. 55 seconds	4.0 cm/sec.

Detergent additions were made during the scouring at rates sufficient to keep the residual grease value at approximately 0.6%. The residual grease was determined by the column-and-tray method[52] at 10 minute intervals (for some lots at 5 minute intervals) to give not less than 12 residual grease results for each lot. The total amounts of soda ash and Glauber's salt added were constant for each lot, viz. 6 lb. (1.5% on the weight of the raw wool) and 16 lb. (4%), respectively.

Initially, some difficulty was experienced with the addition of detergent from dilute solutions stored in overhead tanks. It was found that the detergent separated out from solution, even at fairly mild temperatures. This was not completely unexpected[51], but made it virtually impossible to maintain addition of detergent at a regular rate, since the detergent was no longer uniformly distributed in the stock solution. A further difficulty arose in that even diluted detergent does not disperse readily in the bowls and tends to settle on the bottom. It was decided, therefore, to make additions of detergent from undiluted stock kept in plastic bottles which drip-fed directly into the recirculating pump-line at a point

immediately before the pump. The pump, by its rapid internal circular motion, was able to disperse the detergent very finely and homogeneously in the liquor which was being recirculated.

3.3. Results.

The results obtained in the various scours are given in Table 3. The detergent consumption is given in lb. detergent/100 lb. raw wool for each of the 64 lots, and the average values for the different combinations of rake and roller speeds are also shown. Figures 1 and 2 were drawn using these values.

The percentage figures given in Table 3 are the average percentages of residual grease. They are not exactly identical for all lots, but the differences may be regarded as insignificant, since there is no difference in the trends exhibited by Figs. 1 and 2 when graphs are drawn from values which are statistically corrected to a constant percentage of grease.

3.4. Discussion.

The more generally held view of the washing process at present[9,53] is that the oil on the fibre rolls up into globules when immersed in a detergent solution. These globules can then be removed by a flow of liquor past the fibres such as is produced by agitation or squeezing. The dirt present is also removed in much the same way, as shown by the photomicrographs of Harker[43]. In this case, however, the principal action of the detergent is in swelling the grease-suint-soil complex. This swollen complex is more strongly held to the fibre, but more vigorous mechanical action and faster flow of liquor past the fibre will still remove the complex droplets. The complete washing process consists therefore essentially of two stages:

(a) the formation of droplets of grease-and-detergent complexes, and

(b) the "mechanical" removal of these droplets from the fibres.

It is evident that the rate of flow of liquor past the fibres is an important factor in the scouring of raw wool; hence the belief that the major part of the washing action takes place at the squeeze-rollers where the relative velocity of liquor to wool is considerably higher than elsewhere in the scouring train. For each droplet there will be a certain critical velocity below which it will not be removed; this velocity will depend on such factors as the size of the droplet and the strength of its attachment to the fibre. These factors will vary from one droplet to the next, and one can statistically expect a small number of the complexes to be rather firmly bound to the fibre. As the rate of flow of liquor past the fibres is increased, therefore, it is expected that the number of droplets removed will increase rapidly at first as the critical velocities of the more loosely held ones are exceeded. The rate of removal should slow down as the rate of flow is increased in the higher ranges, since the majority of the drops (the larger ones) have already been removed when this stage is reached.

From Fig. 1 it can be seen that the detergent consumption is generally highest at roller speed 2 r.p.m. The consumption drops on changing to 4 r.p.m. and decreases even further at 6 r.p.m. but may increase at the highest roller speed, depending on the rate of feed. The roller speed can only affect the removal of droplets and the behaviour bears out the conclusions drawn from laboratory work[9,29], i.e. that grease removal increases rapidly at first and then levels off at higher relative speeds of wool to liquor. The only point at which the behaviour becomes anomalous is at a high roller speed combined with a high rate of feed. This

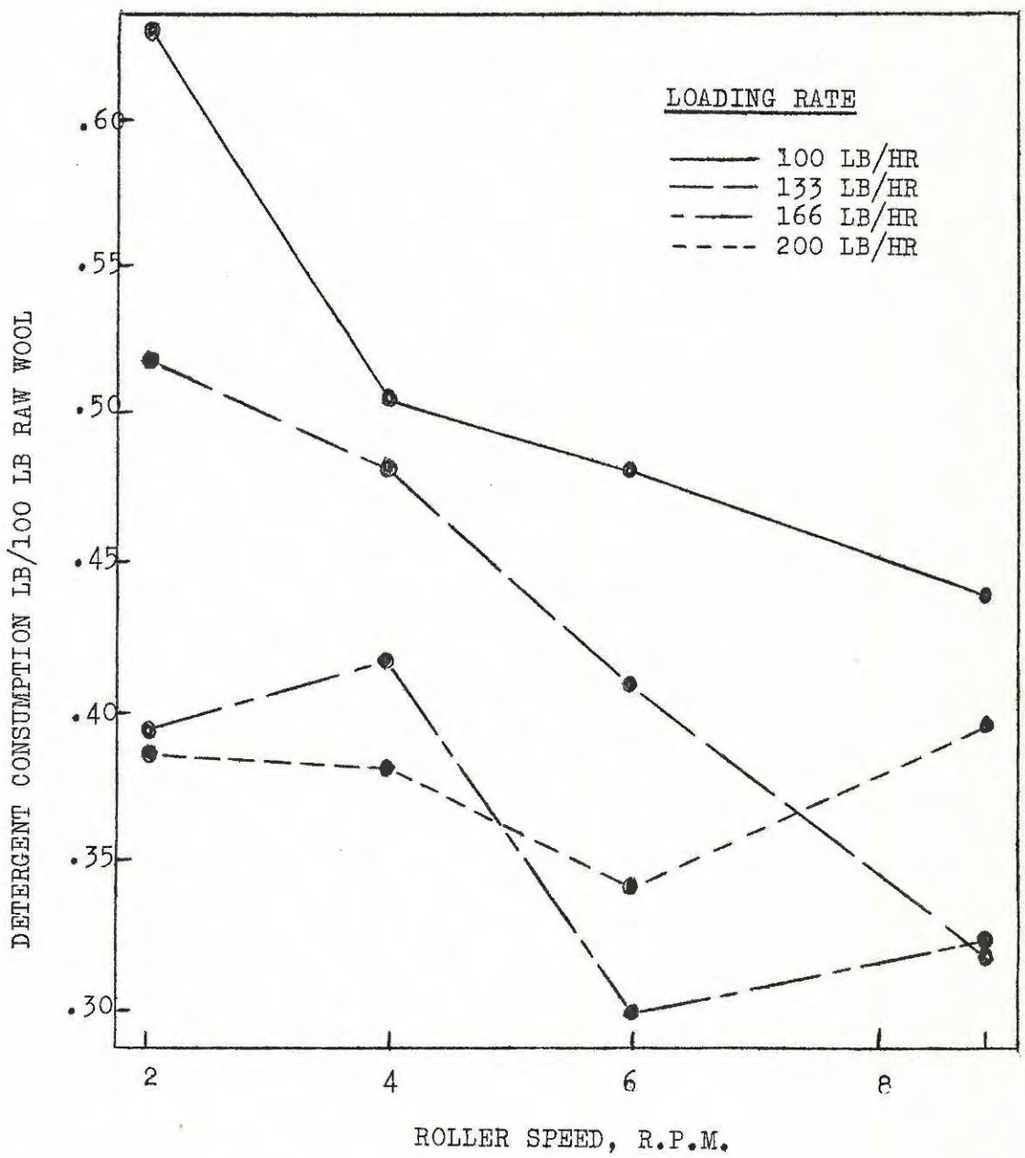


FIG. I.

The effect of roller speed on detergent consumption at different loading rates.

TABLE 3

Amounts of Lissapol (in lb.) required to scour 100 lb. Raw Wool under different mechanical conditions.

LOAD	100 lb./hr.					133 lb./hr.					166 lb./hr.					200 lb./hr.				
Rollers	2	4	6	9	Ave.	2	4	6	9	Ave.	2	4	6	9	Ave.	2	4	6	9	Ave.
Rakes 5	0.635	0.460	0.458	0.448	0.500	0.395	0.313	0.325	0.303	0.334	0.388	0.298	0.310	0.248	0.311	0.273	0.260	0.238	0.368	0.285
	0.66%	0.65%	0.97%	0.59%		0.58%	0.62%	0.60%	0.53%		0.55%	0.62%	0.57%	0.62%		0.70%	0.58%	0.61%	0.51%	
8	0.740	0.478	0.570	0.470	0.565	0.495	0.450	0.393	0.300	0.410	0.455	0.413	0.238	0.253	0.340	0.285	0.378	0.325	0.393	0.345
	0.71%	0.91%	0.66%	0.57%		0.60%	0.64%	0.55%	0.60%		0.75%	0.54%	0.62%	0.65%		0.60%	0.46%	0.62%	0.56%	
11	0.423	0.423	0.415	0.453	0.429	0.580	0.478	0.515	0.335	0.477	0.385	0.430	0.310	0.318	0.361	0.490	0.400	0.303	0.315	0.377
	0.74%	0.56%	0.64%	0.66%		0.71%	0.58%	0.60%	0.65%		0.63%	0.62%	0.58%	0.63%		0.68%	0.56%	0.65%	0.68%	
14	0.750	0.670	0.495	0.388	0.576	0.615	0.695	0.405	0.340	0.514	0.353	0.540	0.338	0.473	0.426	0.505	0.498	0.505	0.518	0.507
	0.52%	0.69%	0.69%	0.59%		0.56%	0.60%	0.63%	0.59%		0.55%	0.63%	0.54%	0.67%		0.62%	0.55%	0.54%	0.58%	
Ave.	0.637	0.508	0.485	0.440		0.521	0.484	0.410	0.320		0.395	0.420	0.299	0.323		0.388	0.384	0.343	0.399	

may be explained by the fact that at the highest rate of feed, the large amounts of wool being presented to the squeeze-rollers impair their action, since the closely packed mass of wool can no longer allow free passage of the liquor. This is a general effect which becomes especially noticeable at the higher roller speeds where the overall decrease in relative velocity of wool to liquor due to this interference would be highest.

An increase in the rate of feed in the lower ranges would mainly affect droplet formation, in that the detergent suspended in the liquors will be used more efficiently when there is a fair amount of wool present in the liquor. Under these circumstances there are more opportunities for contact between detergent and wool. This contact must be virtually exclusively a chance effect since the nonionic detergents have very little affinity for wool fibres[54] and evidence has been presented which supports the view that the presence of a nonionic detergent actually causes preferential sorption of water[55]. Once the high rates of feed are reached, however, there will be increasing effects on droplet removal. At these high rates of feed the mutual interference between the fibres, hindering the free flow of liquor through the body of the wool, becomes an important contributing factor. This would tend to increase detergent consumption by impeding the efficient action of the rollers and to a lesser extent also of the rakes. A stage must be reached where this effect will become dominant in determining the detergent consumption.

The effect of varying the rate of feeding can be seen from Table 3 and Figs. 1 and 2. Detergent consumption is highest at the lowest rate of feed (100 lb./hr.) and drops at 133 lb./hr. and is even lower at 166 lb./hr. The rise in detergent consumption for a rate of feed of 200 lb./hr. is in accordance

with what may be anticipated as above, with the detergent consumption exhibiting the turning point in the vicinity of 166 lb./hr.

The laboratory scouring results mentioned previously[9,28,29] were obtained using ionic detergents; there is very little numerical information available on the nonionics. It is quite likely that this type of detergent could react somewhat differently under plant conditions, especially when changes in rake speeds are made. Faster rake speeds imply faster movement of the wool through the liquors, i.e. shorter immersion times. Since the nonionic detergents are not as readily adsorbed by wool as the ionic types[54,55], it may well be that the time of immersion plays a more important part in the detergent process when considering detergents of the nonionic type. It is obvious then that the rake speed will influence droplet formation by allowing less time and also droplet removal to a certain extent by faster movement of the rakes through the liquor. This increase in relative flow rate of liquor to wool is still far less than that obtained at the squeeze-rollers.

From Fig. 2 it may be seen that the detergent consumption is lowest at a rake speed of 5 s.p.m. and it rises fairly steadily throughout the range considered. Even on changing from 11 to 14 s.p.m., the change is still marked. This is in accordance with the conclusion drawn from the above discussion when the detrimental effect on droplet formation largely outweighs the beneficial effect on droplet removal, which would seem to be the case when it is considered that the time of immersion at the fastest rake speed is 50% less than at the slowest.

From a more practical point of view, it was found that the lowest rake speed (5 s.p.m.) is not practically advantageous,

regardless of the low detergent consumption. This rake speed gives rise to considerable operational difficulty and produces scoured wool with undesirable qualities: it is rather felted and has a brownish colouration. The reason for this seemingly anomalous result becomes obvious when the operating conditions are considered. The low rake speed propels the wool so slowly through the bowls that the wool settles to the bottom. The wool at the bottom of the bowls cannot be moved by the rakes until a fair amount of it has collected. These lumps of wool are then dragged forward by the rakes, which results in the intermittent delivery of large and rather felted lumps of wool to the rollers, which are then not able to operate at maximum efficiency. The brownish colouration of the scoured wool produced at this rake speed is due to sand which settles onto the wool in the bottom of the bowls while the lumps are building up. The sand is then occluded in the interior of these lumps. It is virtually impossible for the rakes or rollers further on in the train to remove this sand from the interior of these lumps. The appearance of the scoured product was considerably better at a rake speed of 8 s.p.m. and even better at 11 s.p.m, with only slight further improvement at 14 s.p.m.

In addition to judging scouring performance on the appearance of the scoured wools they were also compared in their behaviour during carding and combing. The results from this carding and combing study were analysed statistically. The fibre-length analysis after combing did not yield results of great significance; the observed differences resulting from the various changes made during scouring were too small to have any practical value. This may have been due partly to the fact that the

influences of the three factors appeared not to be additive, but to interact in a complicated manner. The analysis of the number of neps produced more significant results. In general, a high loading rate gave the best results; the effects from the other two factors were not significant.

3.5 Conclusion.

It was found that within limits, increasing the squeeze-roller speeds and the rate of feed caused a drop in detergent consumption, whereas an increase in the rake speed caused an increase in detergent consumption.

It must be kept in mind that a certain balance should be maintained between the speeds of the various parts of the scouring set, e.g. too slow a rake speed will cause a break in the ribbon of wool at the rollers and an inordinately high rake speed will cause blocking at the rollers. In view of the above, the optimum running conditions for the plant used in this study may be taken to be a rake speed of 11 s.p.m., roller speed of 6 r.p.m. and a rate of feed of 166 lb./hr. for the type of wool used.

4. THE EFFECT OF BACKFLOW ON THE SCOURING OF RAW WOOL.

4.1 Introduction.

In the scouring of raw wool it is necessary constantly to replace the liquors to prevent them from becoming overconcentrated with insoluble solid matter. Such replacement can be effected by dropping the bowls, but frequent repetition of this process causes considerable loss of production.

The backflow process has the advantage that it makes the scouring process completely continuous by effectively replacing the dirty liquor while the scour is in progress. Water is fed from the rinse bowl to the third bowl, from the third bowl to the second, and so on through the scouring train. Cleaner water starting from the last bowl of the scouring set is therefore moving in the opposite direction to the wool. The only overflow, apart from the excess rinse water, is at the first bowl, where there is an overflow of highly contaminated liquor.

The backflow process has been in use in Europe for some considerable time where scourers are concerned mainly with scouring quality and ease of control. The method has in recent years also been introduced into American mills, especially with the advent of nonionic scouring where it is considered mandatory to use an efficient backflow system in order to preserve the economics and controllability of the scour[10].

4.2 Materials.

In the first series of experiments Lissapol NX was added to the first three bowls and Fluidol W100 (Böhme Fettchemie) was used in the second series. Both are synthetic detergents of the nonionic type. Soda ash (commercial grade sodium carbonate) was

used as a builder in the second bowl.

Two lots of wool were used in the experiments. The first lot consisted of 27 bales of combing type wool, and the second lot was made up of 76 bales of similar types. The clean yields of the lots were 52.7% and 57.4% respectively. The first lot contained 15.5% grease and 10.1% suint, compared with 16.2% and 8.7% for the second lot. (All calculations were based on dry weights.) Both lots were put through a fleece-breaker to open the wool and to facilitate blending. The wool was then carefully blended and re-baled in lots of 200 lb.

4.3 Experimental.

Pilot Plant Operation.

The equipment used was described in Chapter 3. The rate of feeding was fixed at 166 lb./hr., rake speed at 11 s.p.m. and the roller speed at 6 r.p.m. Apart from the changes stated, the scouring procedures were carried out as described before. All lots received identical mechanical treatment, the only variations being in the rates of backflow employed.

The bowl temperatures and initial concentrations of detergents and builders were as in Table 4. All calculations are based on weights as received. The initial concentrations required for an easily controllable scour to 0.6% residual grease was found to be slightly higher for Fluidol W100 than for Lissapol NX.

TABLE 4

Temperatures and initial concentrations

Concentrations are given in per cent, weight/weight

Bowl No.	Temp. °C	Lissapol NX	OR	Fluidol W100	Soda Ash	Glauber's Salt
1	52	0.006		0.009	0.18	-
2	55	0.020		0.022	-	0.35
3	50	0.011		0.015	-	-
Rinse	40	-		-	-	-

Note: The dryer was run at 68°C.

Backflow is defined, for the purposes of this investigation, as the percentage of the total content (170 gallons) of the second bowl transferred to the first bowl in one hour. The same rate of transfer is maintained to and from each bowl in the series, except for the fourth, to which a large quantity of clean rinse water is added. The amount of rinse water added has to be in excess of the highest rate of backflow used to avoid having the rinse bowl depleted faster than it was being added to. The highest rate of backflow employed in the second series of experiments was 200% or 340 gall./hr. The rate of addition of rinse water was therefore kept constant at 400 gall./hr. throughout both series of experiments.

To facilitate the regulation of the rate of backflow, lead-off pipes with two valves were installed on the last three bowls. These lead-off pipes were placed below the false bottoms of the bowls to prevent wool from blocking the valves. The rate of backflow was checked regularly at short intervals.

In the first series of experiments, using Lissapol NX, the rates of backflow used were zero, 38% and 116%. The weight of wool scoured in these experiments was 1000, 2200 and 3600 lb. respectively, giving running times in the pilot plant varying from 6½ hours to 22 hours.

In the second series, using Fluidol W100 as detergent, rates of backflow from zero to 200% at 25% intervals were investigated. The duration of the experiments varied from 6½ hours to 24 hours.

The detergents were added from stock bottles containing undiluted detergent as described before. The stock bottles were weighed at half-hourly intervals for the first three hours of every run and then hourly for the duration of the experiment, in

order to obtain a measure of the rate of addition of detergent under the different conditions.

Residual grease determinations were carried out on the column-and-tray apparatus[56] at approximately five minute intervals, giving a total of about 60 determinations for the shortest run and 240 for the longest experiment. Soda ash was added at a rate just sufficient to keep the pH in the first bowl between 9.0 and 9.5. The pH was checked during the experiment, using universal indicator paper.

The quantities of builders used per 100 lb. of grease wool varied slightly in the different experiments. For soda ash the average consumption was 2.1 lb. per 100 lb. grease wool and for Glauber's salt 4.2 lb.

Initially samples of the scouring liquors were drawn for analysis from the first three bowls, but those taken from the third bowl proved to be relatively free from impurities, the solids in this bowl reaching a maximum at 0.7%. No additional useful information could be obtained from the third bowl samples and it was therefore decided to draw samples from the first two bowls only. Samples were taken every half-hour for the first three hours and thereafter at hourly intervals. During the actual scouring runs, a rough check was kept on the solids content of the liquors, using either a barkometer or a hydrometer.

Laboratory Analyses.

The samples taken during the scouring were tested for pH, total solids content and ether-extractable matter. The pH was measured at room temperature (normally in the vicinity of 20°C) on a Pye laboratory pH meter.

The amount of total solids was determined gravimetrically by taking an aliquot (50 ml.) from the well-shaken sample. This sampling procedure was checked by taking six aliquots from the same bottle after it had been shaken. The results for all six aliquots were in close agreement. The aliquot was placed in a weighed evaporating dish and evaporated to dryness on a boiling waterbath. The residue was then dried to constant weight at 105°C.

After the samples for the gravimetric determinations had been withdrawn the barkometer readings were taken. A barkometer is essentially a hydrometer with different scale markings and is used in the tanning industry. The sample bottles were shaken thoroughly and a sufficient quantity of the liquor was poured into a 500 ml. measuring cylinder. The barkometer was then quickly placed in the measuring cylinder and the reading taken before the solids could settle out.

For the determination of the ether-extractable material, the total solids obtained in the above gravimetric estimation were taken up on wads of fat-free (ether-extracted) cotton wool, which were then placed in extraction thimbles in soxhlets[57] and extracted for four hours with dry diethyl ether.

4.4 Results.

The results obtained have been expressed in graphical form for ease of interpretation. Unless otherwise stated, the graphs were drawn from values obtained during the Fluidol W100 series of experiments which was the more extensive of the two.

Fig. 3 shows the barkometer readings plotted against the amount of total solids as determined by the gravimetric method.

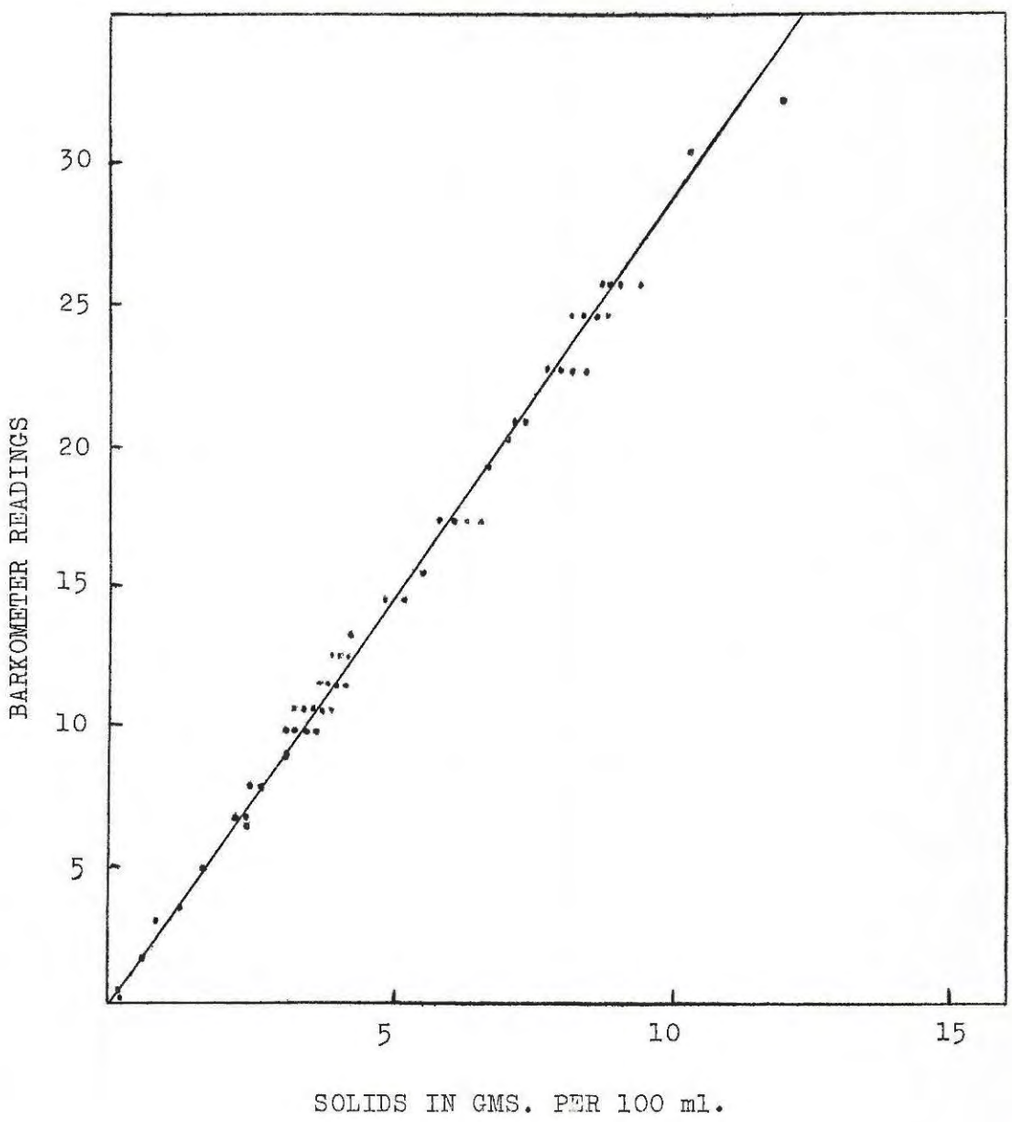


FIG. 3.

Relation between barkometer readings at room temperature and actual total solids content.

Figs. 4 and 5 show the build-up of total solids against time for the first and second bowls respectively and Fig. 6 the build-up of grease in the first bowl. Line F in Fig. 4 represents the build-up of solids against time (in the first bowl) at a backflow rate of 75% for Lox of 33.4% yield. The line is included in the graph for comparison only, since it was obtained in a different experiment which is described in Chapter 5. The points plotted in Fig. 7 show the variation of equilibrium concentration of total solids in the first bowl at different rates of backflow. Fig. 8 shows the effect of different rates of backflow on the consumption of detergent for the two nonionics used in this study.

4.5 Discussion.

From Fig. 3 it may be seen that there is a very close correlation between the amount of total solids determined gravimetrically and the readings on the barkometer. A correlation coefficient of 0.99 was obtained. This method, using the barkometer, is ideal for control in mills, since it is a reasonably accurate gauge of the concentration of solids during scouring. It also has the advantage that it is an extremely rapid method and that measurements can be carried out at any time while the plant is in operation. It should be noted, however, that the barkometer readings and the gravimetric determinations were carried out at room temperature. There is no reason for assuming that similar relationships will not hold at the higher temperatures encountered in the scouring bowls, although a new calibration graph would have to be drawn for use at these elevated temperatures.

From Figs. 4, 5 and 6 it may be seen that at each rate of backflow the concentration of impurities in the bowls increases, fairly rapidly at first, to an equilibrium value at which it stays

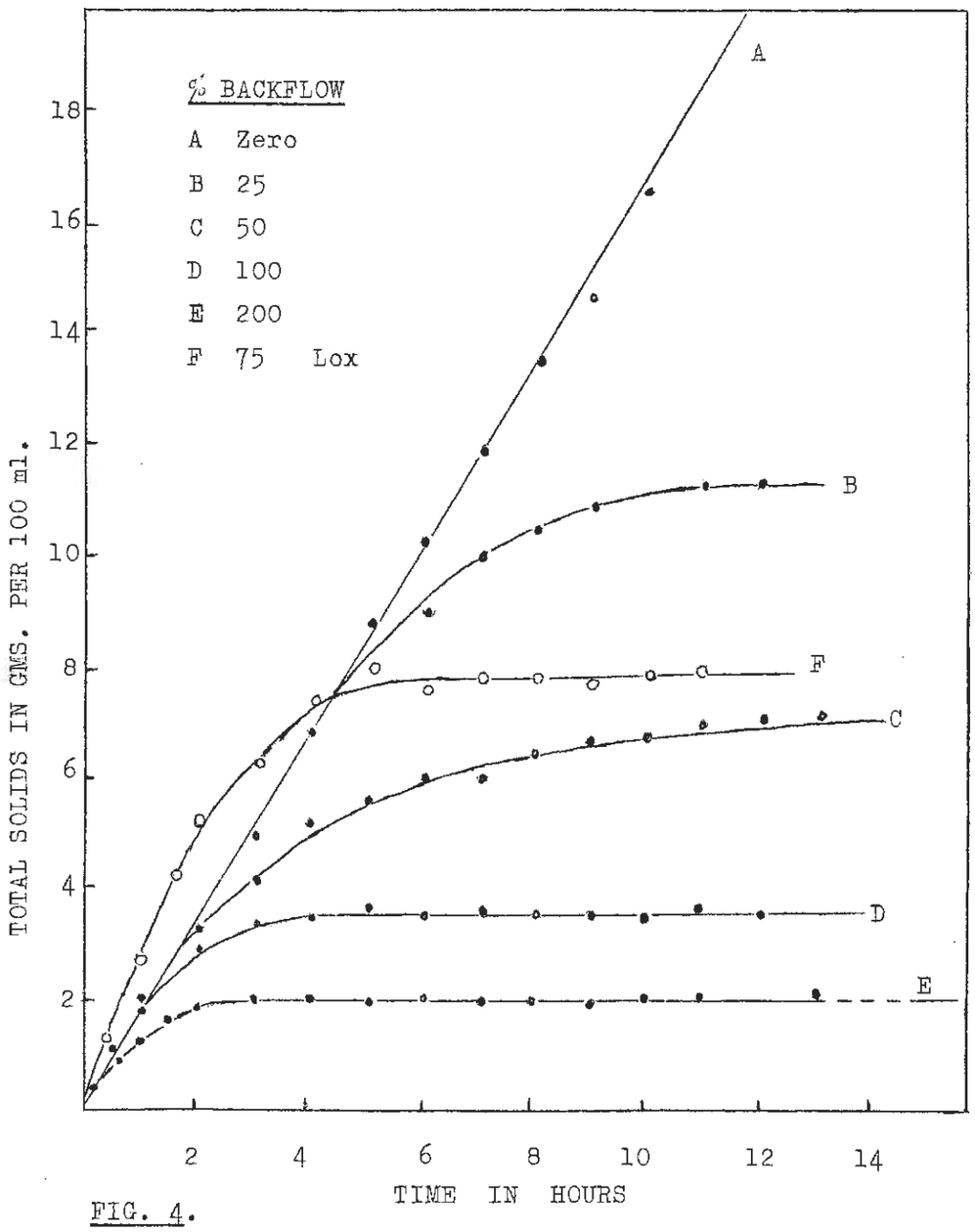


FIG. 4.

Accumulation with time of total solids in the first bowl at different rates of backflow.

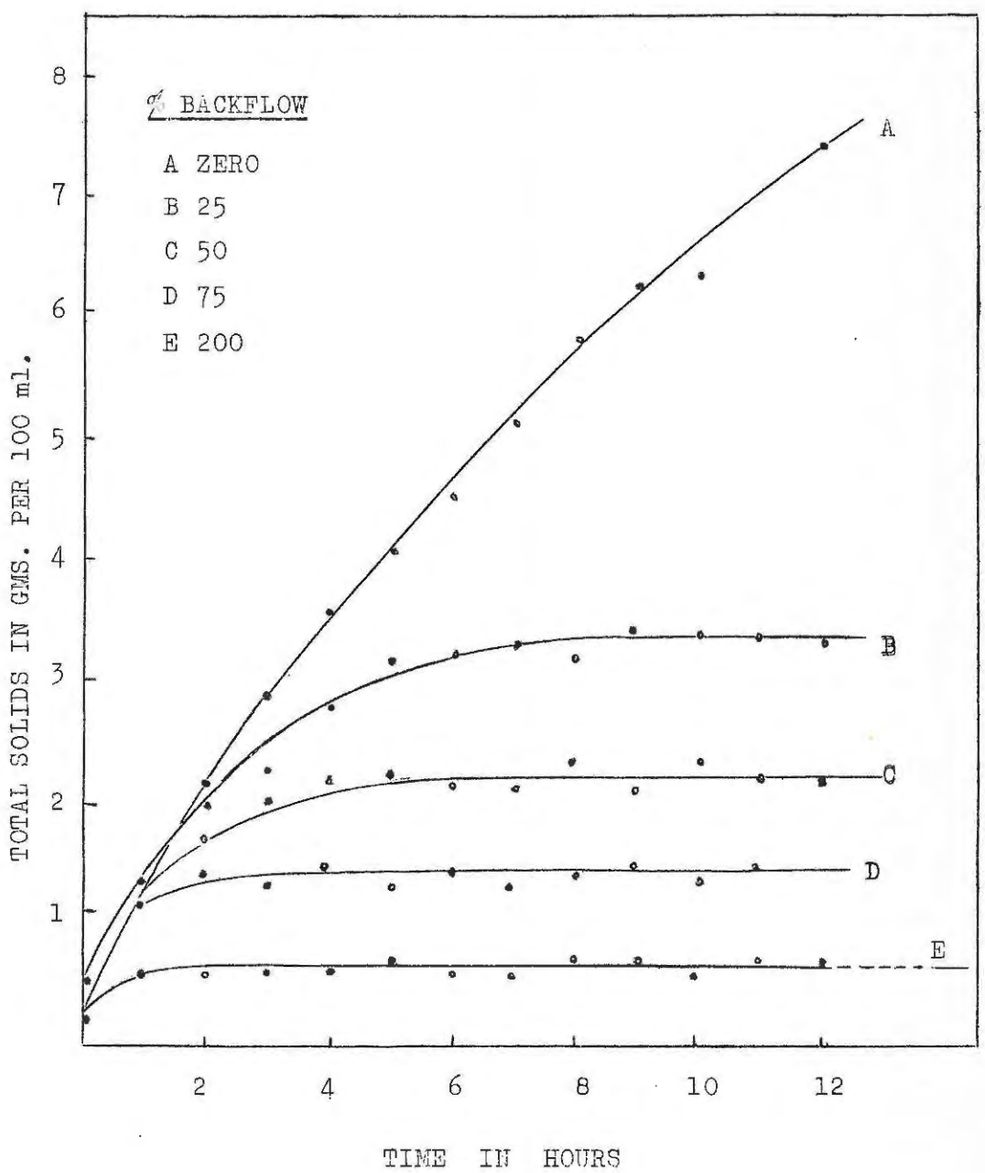


FIG. 5.

Accumulation with time of total solids in the second bowl at different rates of backflow.

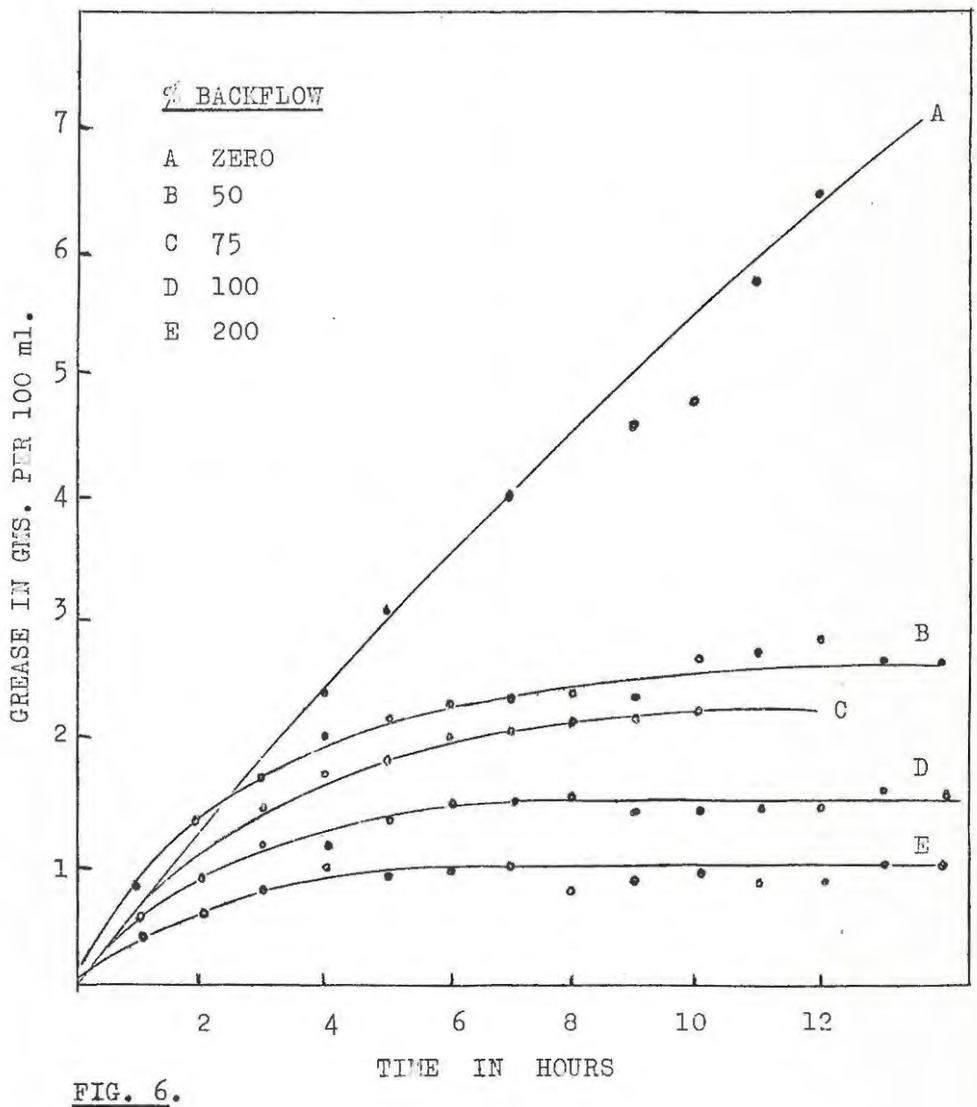


FIG. 6.

Accumulation with time of grease in the first bowl at different rates of backflow.

constant. Even after 24 hours running at 200% backflow, there is no deviation from the constant value (line E in Figs. 4 and 5). The only deviation from this behaviour occurs at zero backflow when the concentration of solids increases in a linear manner with time up to 11 hours (line A in Fig. 4). This is probably an exaggerated case of line A in Fig. 5 and would also start tailing off eventually when the liquor is so dirty that it cannot remove dirt from the wool effectively. The grease content of the first bowl reacts in much the same way (Fig. 6) as does the solids content of the second bowl (Fig.5).

On comparing the maximum total solids in bowls 1 and 2 for given rates of backflow (Table 5), it will be seen that there is a constant relationship between these factors. The solids content of the first bowl is on the average 3.3 times that of the second bowl. From other work[57] it would seem that a solids concentration in the vicinity of 8% is low enough to allow efficient scouring and that 10% solids should be regarded as the maximum permissible concentration. It follows from the above that the concentration of solids in the second bowl would be approximately 2.5% when the first bowl contains 8% solid matter.

TABLE 5.

Maximum total solids at different rates of backflow

% Backflow	Solids in gm./100 ml.		$\frac{\text{Solids}_1}{\text{Solids}_2}$
	Bowl 1	Bowl 2	
25	11.40	3.40	3.35
50	7.10	2.20	3.22
100	3.60	0.95	3.79
125	2.90	0.83	3.50
150	2.50	0.80	3.13
175	2.06	0.70	2.95
200	2.00	0.65	3.08

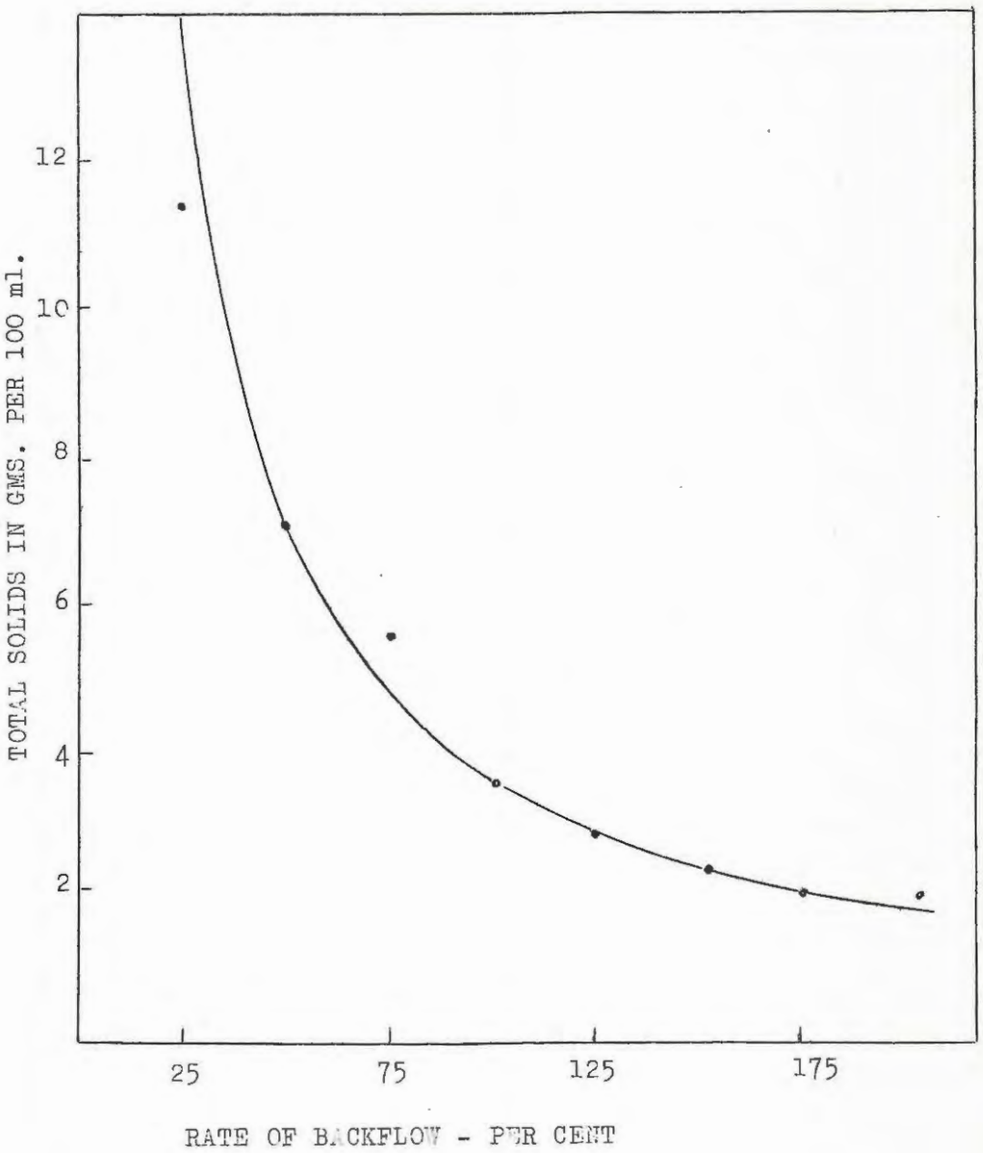


FIG. 7.

The effect of different rates of backflow on the equilibrium total solids concentration in the first bowl.

From line F in Fig. 4 it may be seen that the Lox, which contain a large percentage of dirt, give an equilibrium solids content at 75% backflow of approximately 8%; this value is higher than the figure of 7.1% obtained with the higher yielding type of wool at a lower rate of backflow (50%). It should be noted that this effect is somewhat exaggerated in view of the fact that a slightly faster rate of feed was used for the Lox (200 lb./hr. as against 166 lb./hr. in this series of experiments).

It was found that the equilibrium concentrations of solids in the first bowl was inversely proportional to the rate of backflow used, i.e. maximum solids = K/B .....(4.1)

where B = rate of backflow

K = a constant, the value of which will be determined by the type of wool being scoured. The lower the yield of the wool, the higher the value of K and consequently also the equilibrium solids at a set rate of backflow.

From the experimental results presented in Fig. 4 an average value of K = 363 was calculated.

The points shown in Fig. 7 are the experimental points and the curve was drawn using the calculated value of K. It will be seen that there is excellent agreement between the actual and predicted values.

It now becomes a relatively simple matter to decide on the rate of backflow which would be most suitable under certain conditions once the value of K has been determined. The minimum rate of backflow i.e. the rate of backflow which will give the highest solids concentration at which efficient scouring can still take place, may be obtained from the following relationship:

$$\text{Required rate of backflow} = \frac{K}{\text{Maximum permissible solids}} \quad \ldots\ldots(4.2)$$

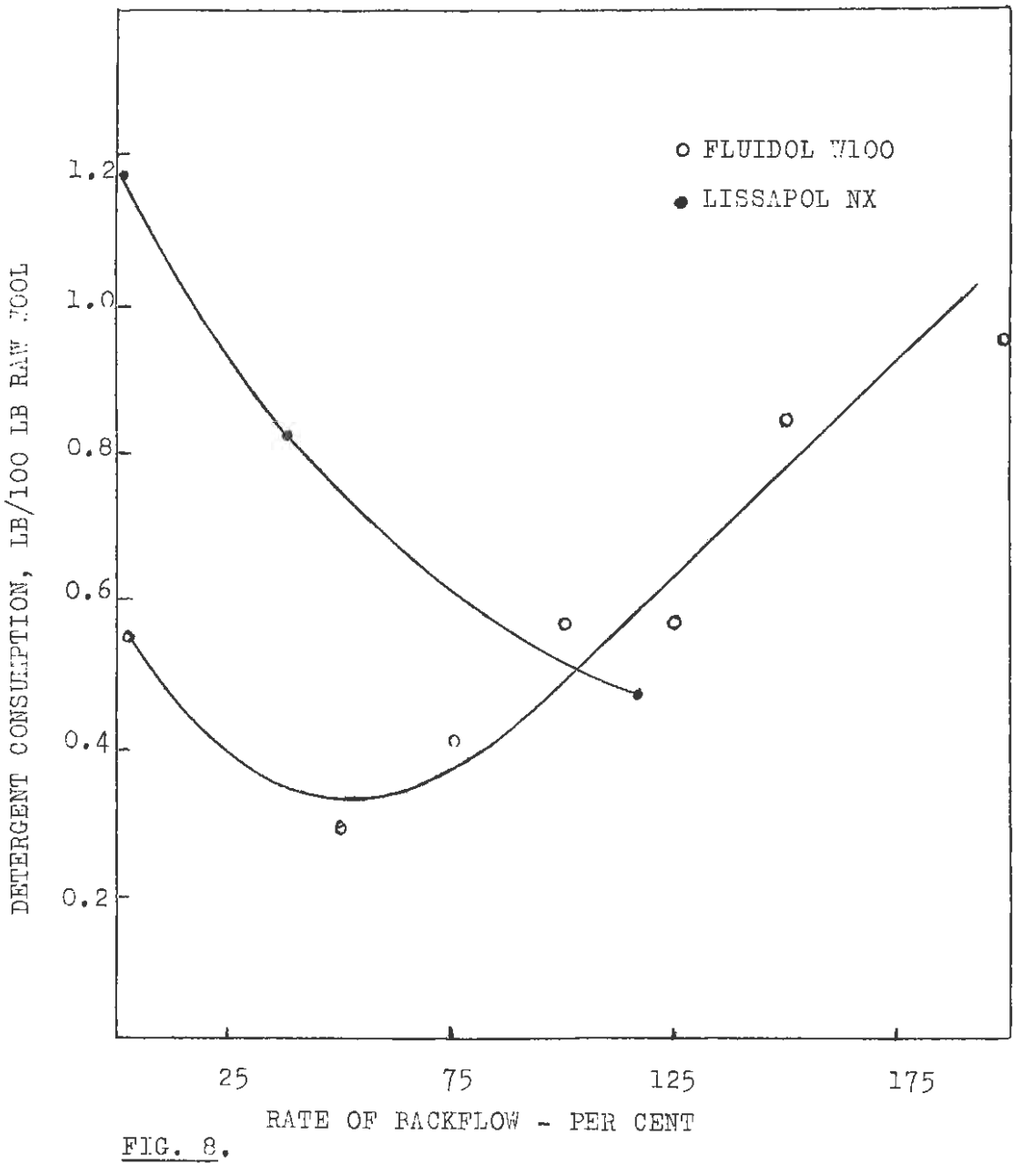


FIG. 8.

The effect of different rates of backflow on detergent consumption.

Fig. 8 represents the detergent consumption in lb./100 lb. raw wool at different rates of backflow for the two detergents used. It will be seen that the consumption of Lissapol NX keeps decreasing down to 116% backflow, whereas the Fluidol W100 curve reaches a minimum at approximately 50% backflow, after which it increases quite rapidly. These results seem rather surprising at first glance in view of the fact that the two detergents are very similar in structure (Lissapol NX is an alkylphenol-ethylene oxide condensate[12] and Fluidol W100 is described as a nonionic detergent based on alkylphenol). In a spot test in the laboratory, their cloud points were found to be 32.9° and 33.4°C, respectively for 0.5% aqueous solutions. Since the cloud points may be taken as an indication of the water solubility of the materials[51], one may conclude that the hydrophile-lipophile balance must be rather similar in both cases.

In a subsequent investigation of the effect of suspended solids in scouring liquors on detergent efficiency (see Chapter 10) it was found that with Fluidol W100 the detergent efficiency started falling off in the vicinity of 7 to 8% total solids. From Table 5 and Fig. 7 it may be seen that at 50% backflow, which is the point of minimum consumption of Fluidol W100, the total solids content of the first bowl is 7.1%. It is therefore thought that in the first part of the Fluidol W100 curve the main effect of increasing the rate of backflow is to decrease the amount of total solids to the point where the detergent can operate efficiently. As the amount of solid matter decreases with an increase in rate of backflow up to 50% the detergent will be used more and more effectively, resulting in a decrease in detergent consumption. After this point has been reached, the main effect of increasing the rate of backflow further is in dumping some of the detergent

through the overflow, causing a loss of detergent and an increase in detergent consumption.

In the case of Lissapol NX, the picture is not as clear as with Fluidol W100, but the same principle may still be applied. In later work (see Chapter 10) it was found that the efficiency of Lissapol NX decreased more gradually over a wider range of solids content, i.e. from 2% to 4%. These solids contents correspond to rates of backflow of 200% to 90% (from Table 5 and Fig. 7). It can be seen from Fig. 8 that the consumption of Lissapol NX decreases from zero backflow down to 116%, at which point it is still decreasing. This means that the point at which the solids content is low enough to allow efficient scouring has not yet been reached, which is in accordance with the above. By analogy with the behaviour of Fluidol W100 it is not unreasonable to assume that the Lissapol NX curve will exhibit similar trends, viz. that the detergent consumption will start increasing once this point is exceeded.

It is clear therefore that a rather higher rate of backflow (lower solids concentration) is required for efficient scouring with Lissapol NX than for Fluidol W100. This is an important factor to be kept in mind by scourers, since the use of an incorrect level of backflow can cause rather large increases in detergent consumption (see Fig. 8).

4.6 Conclusion.

A rapid method for determining the amount of suspended solids in the scouring bowls using a barkometer has been described.

It was found that the equilibrium concentrations of total

solids in the first bowl was inversely proportional to the rate of backflow employed. A fairly constant relationship between the equilibrium solids content of the first bowl and that of the second bowl was observed.

The two detergents used in the study showed widely divergent reactions to variations in the rate of backflow. It was shown that the two detergents required different rates of backflow for efficient scouring and that large savings in detergent could be effected by using the correct rate of backflow for each detergent.

5. THE INFLUENCE OF TEMPERATURE ON THE SCOURING OF RAW WOOL.

5.1 Introduction.

It is commonly agreed that temperature is one of the most important factors in raw wool scouring. The maximum and minimum permissible temperatures are more or less dictated by the properties of the wool and the equipment used.

The minimum temperature used cannot be lower than the melting point of the wool grease, and the viscosity of the grease has also to be borne in mind. Several figures have been quoted for the melting point of wool grease and there has, quite understandably, been a certain amount of variation, mostly included in the range from 40° to 50°C[9,28].

The highest permissible temperature must be consistent with the heat tolerance of the wool and the limitations of the type of plant used[58]. Elevated temperatures may affect the "activity of the alkaline agent" and cause further damage to the fibres[59]. It has been reported[9], however, that at temperatures in the order of 55°C, immersion of greasy or scoured wool in scouring liquors at pH values of up to 11.0 for periods several times longer than those used in scouring practice has no significant effect on the chemical and physical properties of the fibres. It is felt by some workers that the relatively high grease content of the wool as it enters the first bowl affords the fibres a certain amount of protection against degradation by alkali[10].

When scouring with nonionic detergents, it should be kept in mind that these products have a negative solubility coefficient, i.e. they become less soluble as the temperature is increased[51]. It would seem to be accepted, judging from the literature[58] and

the manufacturers' recommendations, that nonionic detergents operate most efficiently at temperatures below or in the vicinity of their cloud points.

This study was aimed at establishing the influence of variation of the temperatures of the first and second bowls on scouring expressly with regard to detergent consumption. The third and fourth (rinse) bowl temperatures were kept constant since it was felt that they play a minimal part in determining detergent consumption. Two series of experiments were carried out on low-yielding Lox, using either Lissapol NX or scouring soap (Lever Brands) as detergent.

5.2 Materials.

The Lox scoured in these experiments was put through a fleece-breaker and then carefully blended to ensure uniform lots. The experimental lots consisted of 1600 lb. wool each. The clean yield of the wool was 35.1% and it contained 9.6% grease and 13.7% suint (all percentages were calculated on dry weights).

The soap, which was supplied in flake form, contained 83% fatty acid, compared to the approximately 60% fatty acid content of the normal bar scouring soap. Soda ash (commercial grade sodium carbonate) was added to the first bowl and Glauber's salt (commercial grade sodium sulphate) was used as a builder in the second bowl. All materials were used as supplied.

5.3 Experimental.

The pilot-scale plant described previously was used in this investigation. The rakes were set at 11 s.p.m. the rollers at 6 r.p.m. and the rate of feed was 200 lb./hr. in both series of experiments. The rate of backflow (see Chapter 4) was kept constant at 75% to give a maximum total solids content of

approximately 8% in the first bowl. Clean water was added to the rinse bowl at a constant rate of 420 gallons per hour throughout. All lots in each series therefore received identical mechanical treatment, the only differences being in the temperatures of the first two bowls.

In the first series the temperatures of the first two bowls were varied in four steps of 5°, from 50° to 65°C, which required sixteen experimental lots to investigate all possible permutations. In view of the fact that the detergent consumption was found to be high at the lower temperatures in the first series, it was decided to scour only nine lots in the second series at temperatures of 55°, 60° and 65°C. The temperatures of the third and fourth (rinse) bowls were kept constant throughout at 50° and 40°C respectively. The Fleissner dryer was run at 67°C.

The initial concentrations were as in Table 6. Calculations are based on weights as received.

TABLE 6

Initial concentrations of reagents in scouring bowls

Bowl No.	Lissapol NX (% w/w)	OR	Soap (% w/w)	Soda Ash (% w/w)	Glauber's Salt (% w/w)
1	0.013		0.059	0.18	-
2	0.033		0.176	-	0.35
3	0.011		0.029	-	-
4	-		-	-	-

Grease determinations were carried out at approximately 5 minute intervals using the column-and-tray[52] method, which gave 80 to 90 determinations per lot. The rate of addition of detergent or soap was determined by the residual grease content of the wool which was scoured to approximately 0.6%

residual grease in both series. Further additions of nonionic detergent were made continuously as described previously. Soap solution (1 lb./5 litres) was added from vertical overhead tanks fitted with graduated sight glasses. The inlet for the soap solution was somewhat larger than for the nonionic detergent, but was also situated on the recirculating pump-line at a point immediately before the pump. In order to prevent the soap solution from solidifying at room temperature, the tanks were fitted with steam heating coils.

Soda ash was added at a rate just sufficient to maintain the pH of the first bowl at 9.0 to 9.5. In the first series, the amount of builder added varied from 1.3% to 1.8% for soda ash and from 2.2% to 2.9% for Glauber's salt. In the second series the soda ash consumption was 0.93% and for Glauber's salt, 1.93%. (Percentages are based on the weights of raw wool.)

5.4 Results.

The consumption of Lissapol NX in lb. detergent per 100 lb. raw wool at various temperatures is given in Table 7. The figures in brackets are the average percentages of residual grease for the respective lots.

TABLE 7

Consumption of Lissapol NX in lb. per 100 lb. raw wool at different temperatures of the first and second bowls

First Bowl Temperature (°C)	50	55	60	65
Second Bowl Temperature (°C)				
50	2.038 (0.81)	0.890 (0.56)	0.475 (0.56)	0.528 (0.60)
55	1.192 (0.66)	0.689 (0.58)	0.424 (0.56)	0.369 (0.58)
60	0.592 (0.59)	0.561 (0.60)	0.333 (0.60)	0.413 (0.61)
65	0.523 (0.59)	0.517 (0.54)	0.318 (0.57)	0.393 (0.53)

The consumption figures for soap in lb. soap per 100 lb. raw wool at various temperatures are given in Table 8 with the average percentages of residual grease for the respective lots in brackets.

TABLE 8

Consumption of soap in lb. per 100 lb. raw wool at different temperatures of the first and second bowls

First Bowl Temperature (°C)	55	60	65
Second Bowl Temperature (°C)			
55	3.91 (0.55)	3.47 (0.63)	3.20 (0.61)
60	3.81 (0.47)	3.06 (0.63)	2.78 (0.59)
65	3.06 (0.61)	3.26 (0.58)	2.92 (0.58)

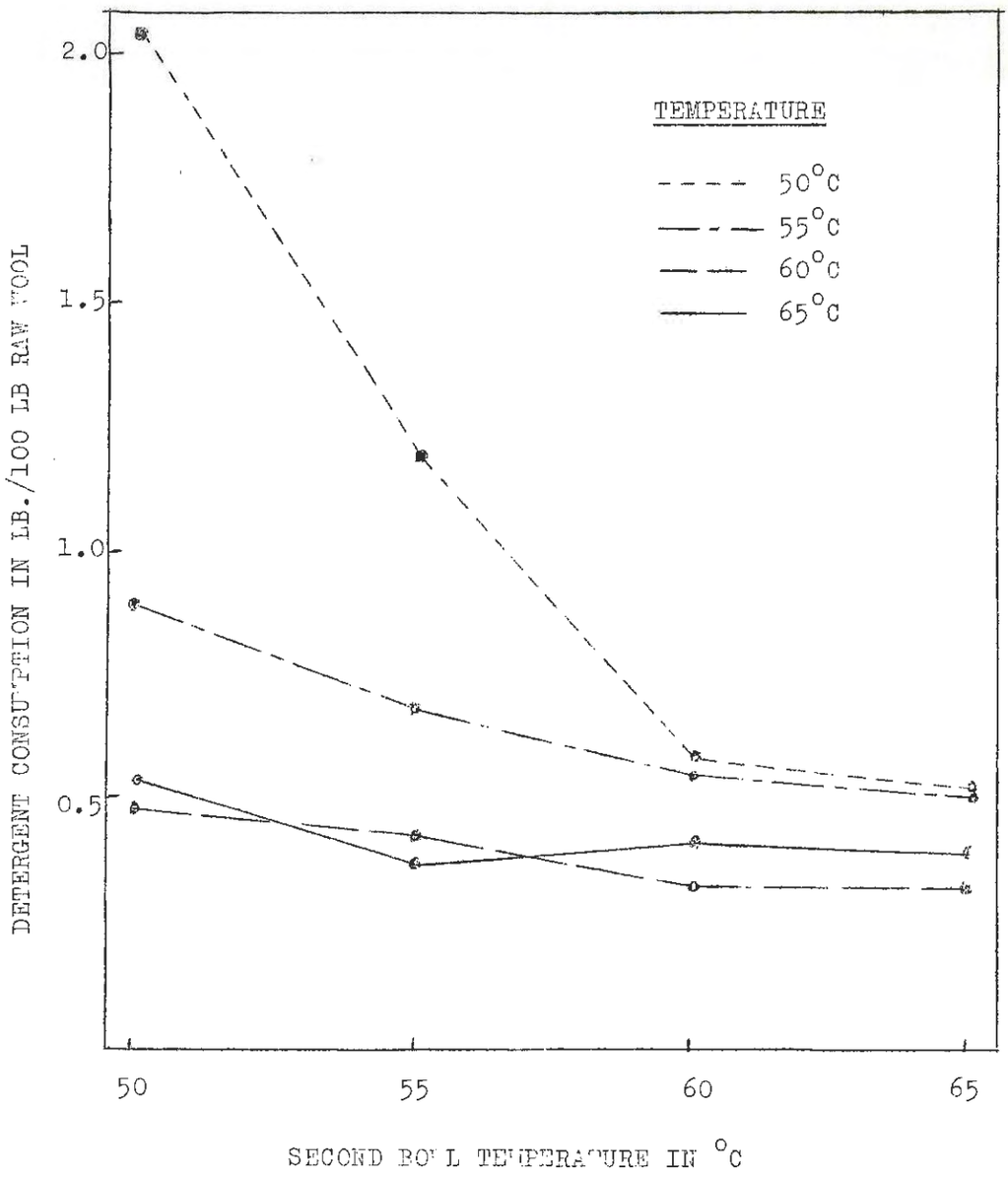


FIG. 9.

Variation of detergent (Lissapol NX) consumption with temperature of the second bowl. Lines are for set temperatures of the first bowl.

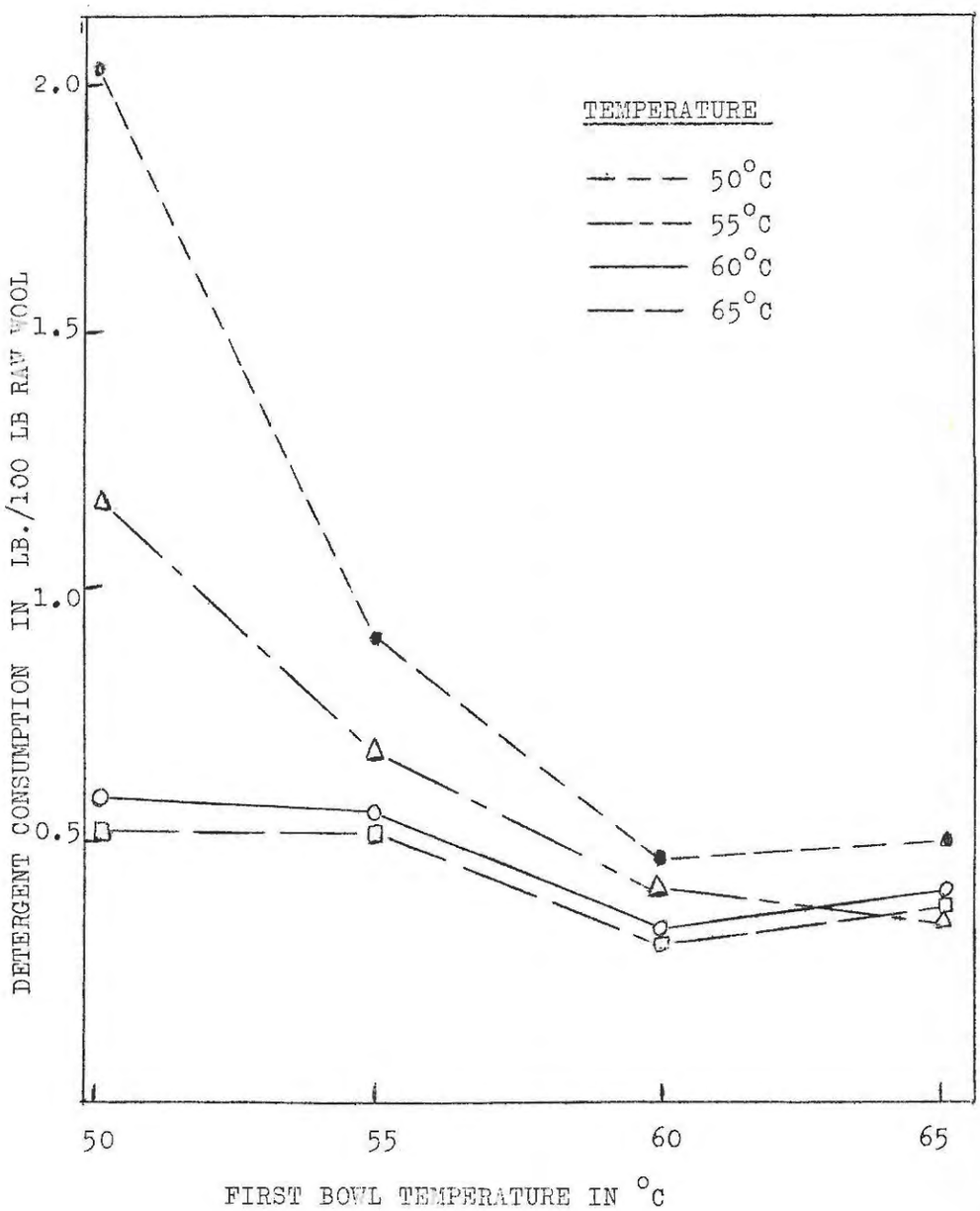


FIG. 10.

Variation of detergent (Lissapol NX) consumption with temperature of the first bowl. Lines are for set temperatures of the second bowl.

The effect of temperature on detergent consumption is shown in Figs. 9,10,12 and 13. Figures 11 and 14 are the response surfaces of detergent consumption (Lissapol NX and soap, respectively) on the temperatures of the first and second bowls.

5.5 Discussion.

There is general agreement in the literature that increased temperature will give rise to more efficient grease removal in view of the fact, amongst others, that viscosity is a temperature-sensitive factor. Also, in the view of Lawrence[30], the large temperature coefficient of detergent processes is a result of the increased rate of diffusion of detergent into the dirt at higher temperatures. Another factor which should be kept in mind is the solubility of the nonionic detergent which decreases with increasing temperature[51]. On the other hand, too high a temperature has been shown to be injurious to wool fibres and seriously affects their behaviour in subsequent processing. Thus, work done by Townend and Tweedie[59] showed that two lots from the same batch of wool scoured at temperatures of 82° and 52°C in the first bowl gave tears of 10.6:1 and 15.2:1 respectively.

The most outstanding feature of the graphs for Lissapol NX (Figs. 9 and 10) is the marked drop in detergent consumption for an increase in the first bowl temperature from 50° to 60°C at a second bowl temperature of 50°C. This effect is actually greater than indicated in Figs. 9 and 10, since the highest point (at 50°C in first and second bowls) was obtained from a lot which had been scoured to 0.81% residual grease. Obviously, if this lot had been scoured to approximately 0.6% grease as were the others, the detergent consumption at this point would have been even higher than indicated in the graphs. It can

further be seen from Fig. 10 that there is very little improvement in detergent efficiency for a temperature increase from 60° to 65°C in the first bowl. This is in accordance with the findings of Anderson and Poulter[22] in their investigation of aqueous jet scouring.

From the lines for 60° and 65°C in Fig. 9, which are almost horizontal, it may be concluded that the temperature of the second bowl is of little consequence at these high temperatures in the first bowl. This could be due to the fact that at these temperatures a large proportion of the grease and dirt is removed in the first bowl, leaving the task of removing the last remnants of dirt, i.e. the smallest globules and complexes, which are more difficult to remove[56], to the second bowl.

As a further aid to the interpretation of the above results, the data was used to estimate a second order response surface[60] of detergent consumption (y) in grams on the temperatures of the first (x_1) and second (x_2) bowls. For convenience in calculation, the temperatures were designated as follows: -3, -1, 1, 3 for 50°, 55°, 60° and 65°C respectively.

The equation of the surface was estimated as

$$y = 186 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + b_5x_2^2 \quad \ldots\ldots\ldots(5.1)$$

where

b_1	= -51.1**	S.E.	8.6
b_2	= -41.4**	S.E.	8.6
b_3	= 17.0**	S.E.	3.9
b_4	= 13.0*	S.E.	4.8
b_5	= 7.8	S.E.	4.8

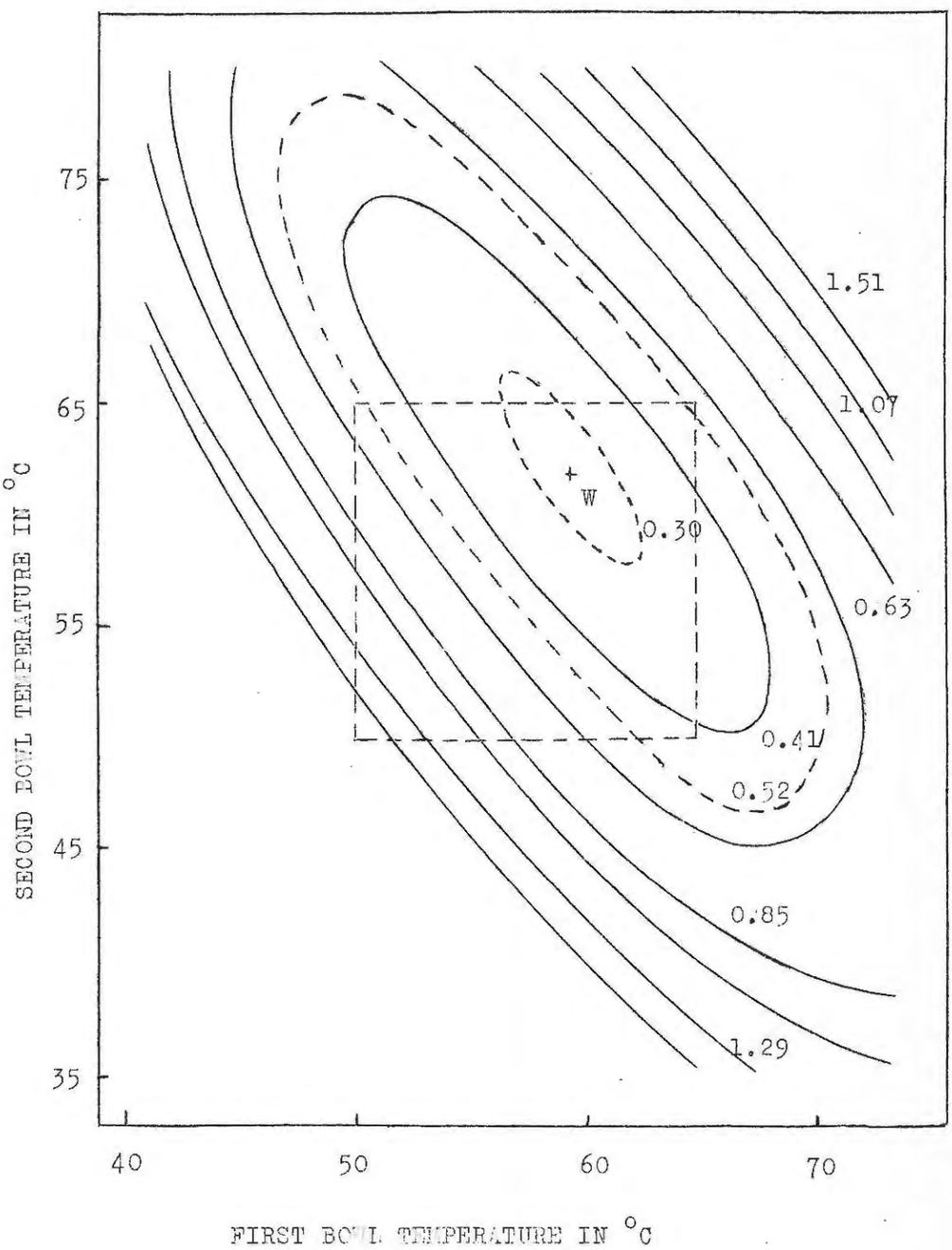


FIG. 11.

Response surface of detergent (Lissapol NX) consumption on the temperatures of the first and second bowls.

With the exception of b_5, all the coefficients are significant. Since b_5 is still nearly twice its standard error it was included in the further calculations. The analysis of variance is given in Table 9.

TABLE 9

Analysis of variance for response surface from Lissapol NX data

Source of variation	d.f.	S.S.	M.S.
Regression	5	521212.95	104242.59
Error	10	59312.80	5931.28
Total	15	580525.75	

The estimated response surface is shown in Fig. 11 with the contour lines indicating the levels of detergent consumption marked in lb. detergent/100 lb. raw wool. It should be kept in mind that the area actually covered by the experimental data is that inside the dotted square, viz. from 50° to 65°C. The rest of Fig. 11 is an extrapolation based on equation (5.1), and is included to give a clearer overall picture. The surface represents a hollow with the lowest point at W where the detergent consumption is 0.285 lb./100 lb. raw wool at a temperature of 59.5°C in the first bowl and 62°C in the second.

The response surface within the limits investigated bears out the conclusions drawn above, i.e. that at high temperatures of the first bowl, the second bowl temperature has little effect on detergent consumption. Similar behaviour is shown when the second bowl temperature is kept constant with the difference that the first bowl temperature

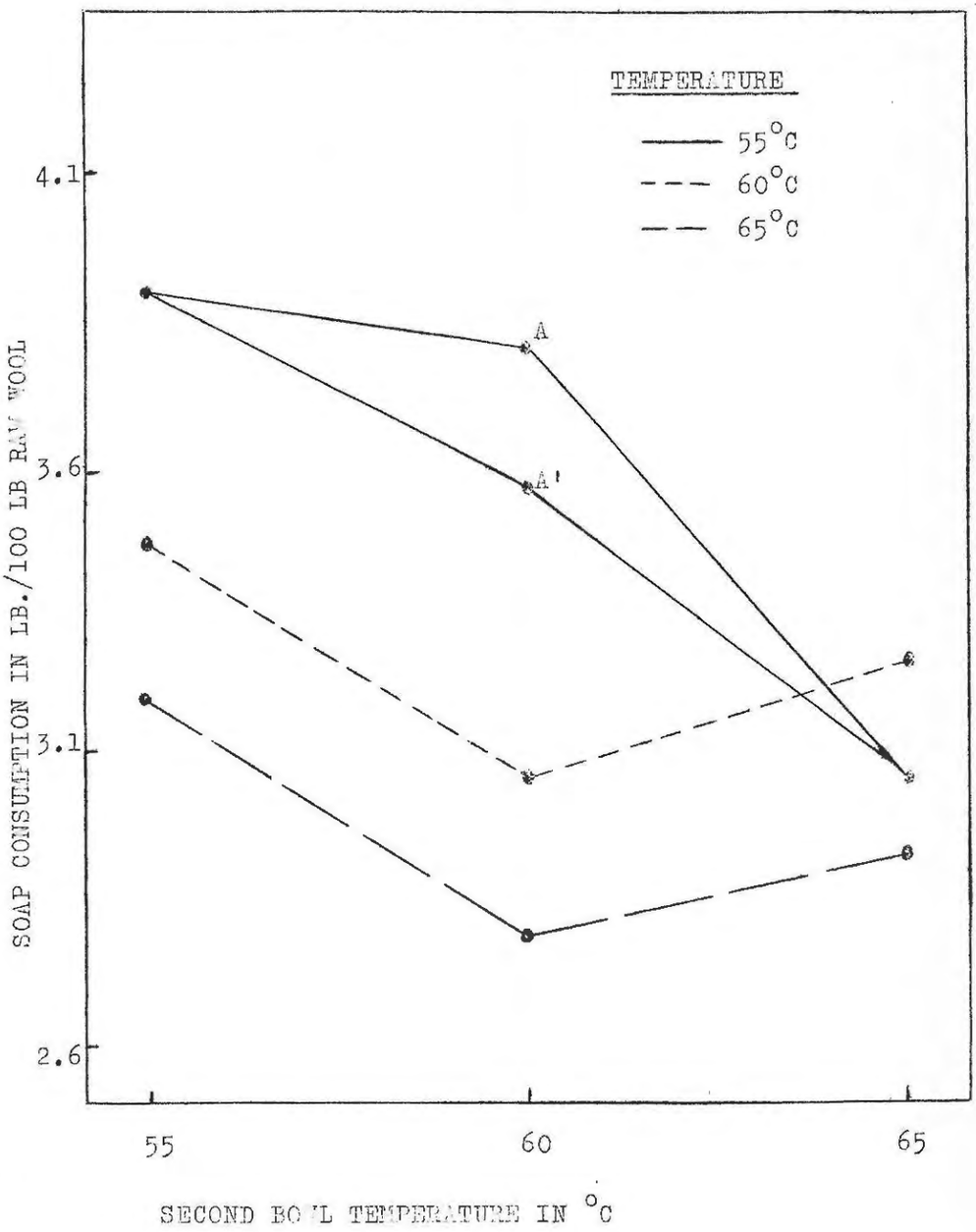


FIG. 12.

Variation of detergent (soap) consumption with temperature of the second bowl. Lines are for set temperatures of the first bowl.

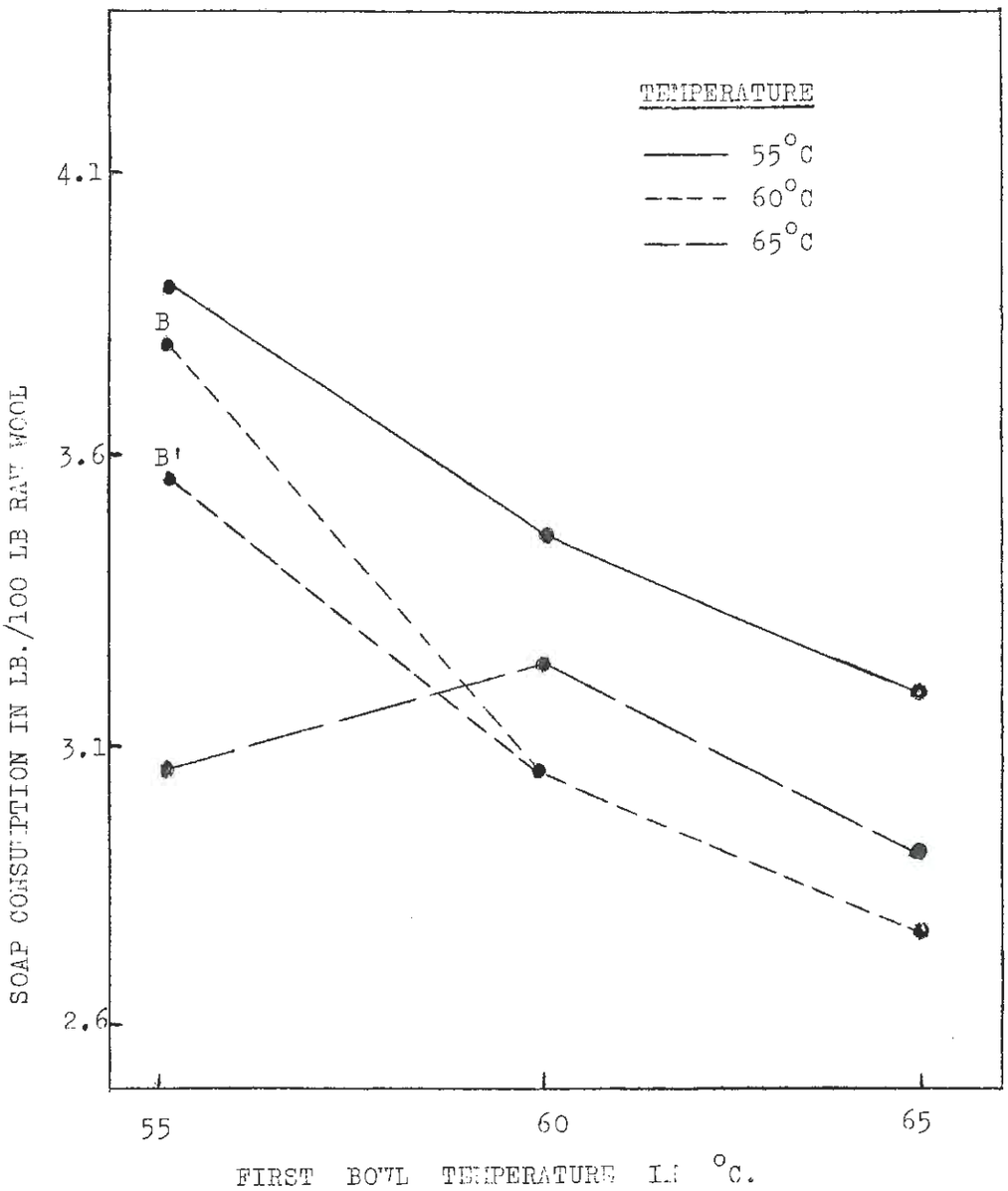


FIG. 13.

Variation of detergent (soap) consumption with temperature of the first bowl. Lines are for set temperatures of the second bowl.

still exerts an effect, even at high temperatures of the second bowl.

An interesting fact which arises from the Lissapol NX data is that, even though it has a cloud point of 34°C, the detergent consumption only reaches a minimum in the vicinity of 60°C, after which it starts increasing.

Figs. 12 and 13 are the consumption curves for soap. The points A and B on the graphs are higher than would be expected because this lot was scoured to 0.47% residual grease, compared with approximately 0.6% for the other lots. The value read off from the response surface at this point is 3.57 lb./100 lb. raw wool. This is the figure which is denoted by A' and B' in Figs. 12 and 13. The decrease in detergent consumption in both graphs is generally greater from 55° to 60° than from 60° to 65°C. Neither of the bowls play a dominating part in determining the detergent consumption.

A response surface was obtained for soap consumption (y) on the temperatures of the first (x_1) and second (x_2) bowls. The temperatures were coded as follows: 55°C(-1), 60°C(0), 65°C(+1). The equation of the surface was estimated as

$$y = 3.2517 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + b_5x_2^2 \quad \ldots\ldots\ldots(5.2)$$

where

b_1 = -0.313 S.E. 0.13

b_2 = -0.2233 S.E. 0.13

b_3 = 0.1425 S.E. 0.16

b_4 = 0.005392 S.E. 0.13

b_5 = 0.02873 S.E. 0.13

The analysis of variance was as in Table 10.

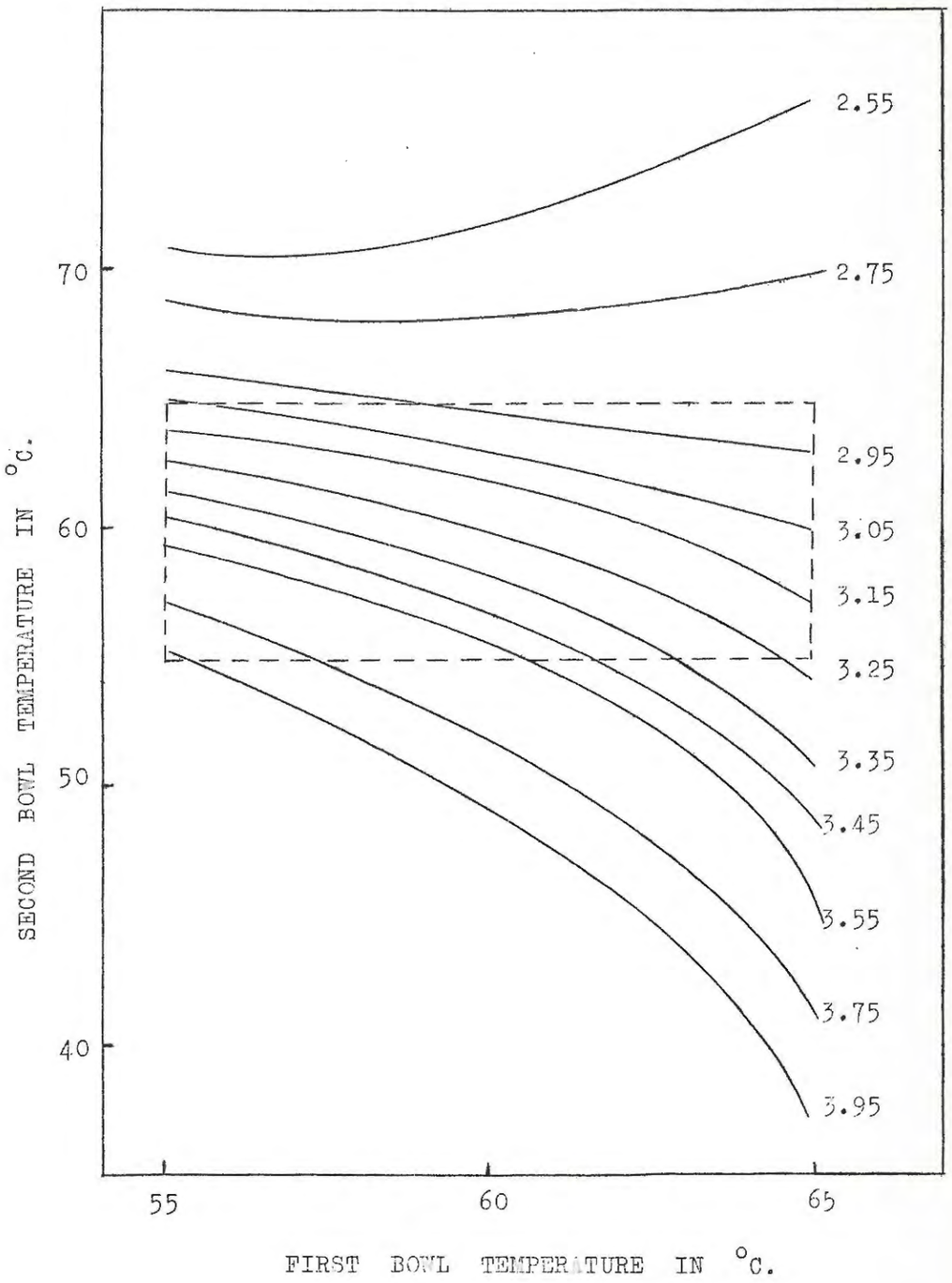


FIG. 14.

Response surface of detergent (soap) consumption on the temperatures of the first and second bowls.

TABLE 10

Analysis of variance for response surface from data for scouring soap

Source of variation	d.f.	S.S.	M.S.
Regression	5	0.898539	0.177707
Error	3	0.298283	0.09942767
Total	8	1.196822	

The estimated response surface is shown in Fig. 14 with the contour lines which show the levels of soap consumption marked in lb. per 100 lb. raw wool. It is clear from Fig. 14 that in the case of soap there is no point of minimum consumption within the temperature range 55° to 65°C. This is in accordance with the work of Veldsman[28] who compared sodium cetyl sulphate with soap and found an eventual decrease in efficiency with temperature for sodium cetyl sulphate but none for soap.

Again, the area within the dotted rectangle is that part of the response surface covered by experimental results, the rest of the surface being an extrapolation to clarify the picture. It will be seen from Fig. 14 that increases in the temperatures of either of the two bowls cause a marked decrease in detergent consumption in the lower ranges, the differences being reasonably similar in both cases.

In the higher ranges it was also found that considerable decreases in detergent consumption occurred at a constant first bowl temperature of 65° when the temperature of the second bowl was increased from 55° to 65°C. Variations were, however, relatively smaller for a corresponding increase in the temperature of the first bowl when that of the second was maintained at

65°C.

5.6 Conclusion.

An increase in temperature in the lower ranges in either of the first two bowls caused a marked decrease in detergent consumption. This effect was less marked in the region 60°C to 65°C. When using a nonionic detergent the first bowl temperature was found to be the dominant factor in determining the detergent consumption.

From the two response surfaces estimated for detergent consumption on temperature it was concluded that there was a point of minimum detergent consumption in the case of the nonionic detergent, whereas with soap no such minimum was found in the temperature range investigated.

6. COMPARISON OF DETERGENTS FOR RAW WOOL SCOURING.

6.1 Introduction.

The wool scourer faces a difficult task when he has to make a choice of a suitable detergent from the large number which are offered to him. This study was aimed at comparing a number of detergents which could be considered for wool scouring. Of the eleven detergents compared in each series of experiments, the majority were of the nonionic type, but soap and one other anionic detergent were also included. The detergents were compared with regard to consumption and cost. The scouring costs were calculated on the same basis for all detergents viz. the price per lb. in 2,000 lb. lots, f.o.r. Port Elizabeth. The costs obtained are relative, in that the only factor considered was the actual price of the detergent, all other factors being similar for each lot scoured.

6.2 Materials.

The detergents were used as supplied by the manufacturers, the soap being supplied in flake form which contained 83% fatty acid. Soda ash (commercial grade sodium carbonate) was added to the first bowl and Glauber's salt (commercial grade sodium sulphate) was used as a builder in the second bowl.

Bulk lots of Lox and fleece wool were opened and blended separately before scouring. The Lox which had a clean yield of 36.2%, and contained 9.6% grease and 13.7% suint, was used in the first series of experiments in which 1,600 lb. of the blended wool was scoured with every detergent. Similarly, 1,000 lb. lots of blended fleece-wool with a clean yield of 52.3%, 10.6% grease and 8.1% suint were scoured in the second series. (All

figures are based on dry weights).

6.3 Experimental.

The pilot plant described in Chapter 3 was used in this study. The rakes were set at 11 s.p.m. and the rollers at 6 r.p.m. Rates of feed of 266 lb./hr. and 166 lb./hr. were used for Lox and fleece-wool respectively in order to maintain a reasonable production figure which would be approximately similar for both lots (96 lb. and 87 lb. scoured wool per hour, respectively).

The rate of backflow (Chapter 4) was set at 150% for the first series and 75% for the second. These rates gave sufficiently low concentrations of total solids in the first bowl for continuous scouring without the danger of redeposition of dirt onto the wool. Clean water was added to the rinse bowl at a constant rate of 420 gall. per hour.

Soda ash was added to the first bowl at a rate just sufficient to keep the pH between 9.0 and 9.5. The pH was checked at regular short intervals using universal indicator paper. The temperatures, which were kept constant for all lots in each series, were as follows:

	First series	Second series
First bowl	60°C	55°C
Second bowl	55	55
Third bowl	50	50
Fourth bowl	40	40
Dryer	67	65

Table 11 gives the initial charges of detergents in each bowl. (The fourth bowl was used as a clean rinse bowl). It will be seen that for most nonionic detergents, similar initial charges could be used, but considerably higher concentrations were

required to obtain an easily controllable scour to 0.6% residual grease in the case of the anionic detergents. The initial charges of builders in the bowls were the same in all experiments, viz. 3 lb. soda ash in the first bowl and 6 lb. Glauber's salt in the second.

TABLE 11

Initial charges required for different detergents

Detergent	Source	Series	1st Bowl (lb.)	2nd Bowl (lb.)	3rd Bowl (lb.)
NONIONIC					
Lissapol NX	I.C.I.	1	0.25	0.52	0.14
		2	0.16	0.52	0.23
Fluidol W100	Böhme Fettchemie	1	0.31	0.62	0.15
		2	0.21	0.48	0.18
Triton X100	Rohm & Haas	1	0.29	0.72	0.26
		2	0.21	0.52	0.29
Triton N100	Rohm & Haas	1	0.32	0.78	0.21
		2	0.20	0.62	0.19
Nonidet P40	Shell Chemicals	1	0.23	0.74	0.18
		2	0.20	0.53	0.16
Nonidet P 80	Shell Chemicals	1	0.40	0.74	0.41
OCC 50	Shell Chemicals	2	0.22	0.44	0.21
Berol Lanco	Berol Aktiebolag	1	0.22	0.65	0.15
		2	0.15	0.48	0.19
Tergitol TP9	Union Carbide	1	0.28	0.78	0.28
		2	0.20	0.50	0.16
Tergitol NPX	Union Carbide	1	0.29	0.75	0.25
Tergitol 12P12	Union Carbide	2	0.15	0.40	0.16
Tergitol 12P9	Union Carbide	2	0.17	0.46	0.15
ANIONIC					
Soap	Lever Brands	1	1.00	3.00	0.50
		2	1.00	3.00	0.50
Adipon D Kz.	Böhme Fettchemie	1	1.10	3.31	0.66

Further additions of nonionic detergents were made continuously from undiluted stock in overhead containers as described elsewhere. The two anionic detergents, soap and Adipon D Kz. had to be dissolved in water (1 lb. per 5 litres) and were added from the larger tanks as described in Chapter 5. The total amounts of soda ash and Glauber's salt used were identical for all lots in each series, being 1.1% and 2.5% respectively for the first series and 1.9% and 2.5% in the second. (Percentages calculated on the weights of raw wool scoured).

For most of the detergents additions were started after 15 minutes running time, but in some cases the required residual grease value of 0.6% demanded the first additions to be started simultaneously with the feeding of raw wool into the set. In some cases it was not possible to add sufficient detergent to keep the residual grease down to 0.6% because of practical considerations. (See further under para. 6.5).

The residual grease determinations were carried out at 5 minute intervals on the column-and-tray apparatus[56].

6.4 Results.

Table 12 contains the results obtained in the first series of experiments on the scouring of Lox and Table 13 the results obtained with fleece wool.

The costs are calculated on the basis of prices per lb. of detergent in 2,000 lb. lots, f.o.r. Port Elizabeth (South Africa). The costs given in the Tables are the costs in South African cents (10 cents = 12 pence stg.) of scouring 100 lb. raw wool. These figures take into account only the actual cost of the detergents.

TABLE 12

Detergent consumption and costs for scouring Lox. (First Series)

DETERGENT	Residual grease %	lb. detergent used per 100 lb. raw wool	Cost of detergents in cents per lb.	Cost of scouring 100 lb. raw wool in cents
Tergitol TP9	0.65	0.739	15.5	11.45
Berol Lanco	0.66	0.864	15	12.96
Lissapol NX	0.60	0.798	17	13.57
Triton N100	0.64	0.917	16	14.67
Nonidet P40	0.65	0.818	19.5	15.95
Fluidol W100	0.59	0.995	20.5	20.40
Tergitol NPX	0.79	1.367	15.5	21.19
Triton X100	0.69	1.351	16	21.62
Soap	0.70	3.204	8.16	26.14
Nonidet P80	1.19	2.050	21.5	44.08
Adipon D Kz.	0.79	2.895	23.98	69.42

TABLE 13

Detergent consumption and costs for scouring fleece-wool.(Second Series)

DETERGENT	Residual grease %	lb. detergent used per 100 lb. raw wool	Cost of detergents in cents per lb.	Cost of scouring 100 lb. raw wool in cents
Tergitol TP9	0.58	0.773	15.5	11.98
Tergitol 12P12	0.60	0.797	15.5	12.35
Tergitol 12P9	0.57	0.804	15.5	12.46
Lissapol NX	0.60	0.767	17	13.04
Soap	0.62	1.840	8.16	15.01
Triton N100	0.59	1.087	16	17.39
Triton X100	0.61	1.134	16	18.14
Berol Lanco	0.59	1.339	15	20.08
Nonidet P40	0.58	1.114	19.5	21.72
OCC 50	0.54	0.969	23.2	22.48
Fluidol W100	0.56	1.113	20.5	22.82

6.5 Discussion.

It will be seen that some of the residual grease values in Table 12 are appreciably higher than 0.6%. It was found impossible to scour these lots to lower grease values without considerable operational difficulty. With a high concentration of detergent in the scouring bowls, the wool slipped at the squeeze-rollers, causing them to become blocked which in turn caused stoppages and loss of production. Undesirable excessive foaming also took place at these high concentrations. The detergents which gave rise to these difficulties were not included in the second series of experiments (see Table 13). It should be borne in mind that the detergents which gave a residual grease content of appreciably more than 0.6% would tend to be flattered by the comparison.

In the study on backflow (Chapter 4), it was found that detergents which are similar in physical and chemical structure react very differently with respect to detergent consumption under different backflow conditions. This kind of deviation could have a marked influence on the results of a study such as the present one. It would have been totally impractical to attempt to establish the optimum backflow conditions for each detergent separately, and the trials were therefore conducted under conditions which should prevail in a scouring mill when these types of wool are being scoured. A high rate of backflow was selected for the first series in view of the low yield of Lox and a somewhat lower rate was used in the second series.

The temperature of the scouring bowls is an important factor in determining the efficiency of a specific detergent.

Hydrogen bond formation takes place when nonionic detergents containing ethylene oxide groups are dissolved in water. Increasing the temperature of the solution progressively destroys these hydrogen-bonds, leaving the detergent with a smaller effective hydrophilic residue. As a result the solubility of the nonionic is reduced and the phenomenon of clouding is observed[51]. The nonionic detergent which has become more strongly hydrophobic at the elevated temperatures employed in the scouring experiments will now have an affinity for the grease which covers the surface of the wool fibres and will be more readily adsorbed onto it.

Some workers[58], including manufacturers, seem to be of the opinion that nonionic detergents can be employed most effectively at temperatures below or in the vicinity of their cloud points, whereas others[61] regard a high proportion of hydrophobic material in the detergent molecule as advantageous to scouring. Other work has shown that nonionic detergents can function effectively at temperatures considerably above their cloud points, either as a wetting agent under the conditions of the Draves test[62,63], or as a detergent[27]. At the scouring temperatures used in this study the rate of diffusion of detergent into the dirt will be high[30], so that the removal will take place readily and fairly rapidly.

It is interesting to note the difference in behaviour and cloud point (c.p.) of the following pairs of detergents (see Table 12): Nonidet P40 (c.p. 47°C) and Nonidet P80 (c.p. 80°C); Tergitol TP9 (c.p. 51°C) and Tergitol NPX (c.p. 63°); and from Table 13, Tergitol 12P9 (c.p. 18°C) and Tergitol 12P12 (c.p. 60°C). In each pair, the hydrophobic unit of the molecules is identical, the only difference being in the lengths of the hydrophilic ethylene oxide chains. It will be seen that each pair contains

one detergent with a cloud point above the scouring temperatures; the other has a lower cloud point. Consumption was found to be lower for the detergent with the lower cloud point. The only slightly lower molecular weights of the lower clouding detergents cannot account for the considerable differences in detergent consumption.

In the case of Tergitol 12P12 and 12P9 there is an exceptionally large difference in cloud point and in this particular case the higher clouding detergent was slightly more efficient. Here the scouring temperatures were 39°C higher than the cloud point of Tergitol 12P9. It is thought that when detergent solutions are used at temperatures this far above their cloud points, the detergent becomes too hydrophobic and is present in the liquors in a form unsuitable for scouring.

It should be kept in mind throughout the discussion following that there were certain dissimilarities between the treatments accorded the two scouring lots:

a) The first lot (Lox) was scoured at 60°C in the first bowl, compared with 55°C for the second lot (fleece-wool). This difference would have the effect of lowering the detergent consumption for Lox relative to that obtained for fleece-wool.

b) The pH of the first bowl was kept at 9.0 to 9.5 for both series and it will be seen that the Lox required less soda ash than the fleece-wool (1.1% vs. 1.9%), due to the fact that the Lox was more alkaline than the fleece-wool[64]. Later work (Chapter 7) indicates that this difference would also influence the detergent consumption. It is expected that the detergent consumption for Lox would be increased relative to that of fleece-wool.

Although it is unlikely that these two opposite effects would cancel each other exactly, it is thought that the nett effect would not have serious effects on the conclusions drawn and it should be pointed out that the actual comparisons drawn between the two lots refer only to very large differences in detergent consumption which could not be due solely to one of the above differences.

A point of significance which arises from Tables 12 and 13 is the reaction of the two different types of wool to scouring with the two types of detergent. In the case of soap, which is an anionic detergent, the amount used for scouring Lox is almost twice that required to scour the same weight of fleece-wool. This can be ascribed to a loss of soap due to its tendency to become adsorbed onto the wool and impurities present in the liquors[54]. This effect should be most marked in the scouring of Lox which contains a large percentage of dirt. The nonionic detergents, on the other hand, show an approximately constant detergent consumption for both types of wool. This is in accordance with the remarkable reluctance of this type of detergent to become adsorbed onto wool[54,55] (and presumably also onto dirt present in the scouring liquors). The consumption of nonionics tended, in fact, to be slightly higher for fleece-wool than for Lox, which can perhaps be attributed to the fact that the fleece-wool contained 1% more grease than the Lox (10.6% vs. 9.6%). This difference is quite small and could even be due to the effect of factors a) or b) above. The above effects are reflected in Tables 12 and 13 where it may be seen that when scouring Lox, eight of the non-ionics investigated could be used more economically than soap and in the case of fleece-wool only four of the nonionic detergents

were more economical than soap.

6.6 Conclusion.

Several detergents were compared for scouring efficiency under fixed conditions using two types of wool. It was found that nonionic detergents could be used at considerably lower cost than soap when scouring low-yielding Lox. For a higher-yielding type of wool, soap became more competitive economically. The consumption of nonionic detergents remained relatively constant for both types of wool scoured, but the consumption of soap was markedly greater for Lox than for fleece-wool.

The nonionic detergents generally operated more efficiently when the scouring temperatures were higher than the cloud points of the detergents. This effect was observed with both types of wool used, but it was more noticeable in the case of Lox.

A very high detergent concentration was required in certain cases in order to scour raw wool to a 0.6% residual grease level. As a result, excessive foaming occurred and further inconvenience was caused by blockages at the squeeze-rollers. These detergents were therefore regarded as unsuitable for raw wool scouring.

7. THE EFFECT OF DETERGENCY BUILDERS ON THE SCOURING OF RAW WOOL.

7.1 Introduction.

It has been known for some considerable time that the addition of electrolytes to scouring liquors cause an appreciable increase in detergent efficiency[31,65,66], even though these electrolytes have no detergent power on their own. Amongst the electrolytes in industrial use today are common salt (sodium chloride), Glauber's salt (sodium sulphate) and soda ash (sodium carbonate).

When scouring with soap, it is considered essential[7,66] to maintain the pH in the vicinity of 10 to avoid the liberation of free fatty acids and the subsequent decrease in detergent efficiency. Soda ash is normally used for this purpose, although potassium carbonate and sodium silicates and phosphates have also been found suitable[35]. The original theory[10] that alkali assisted the scouring process by saponification of a portion of the wool grease was shown to be incorrect when it was found that only a small proportion (0.5%) of wool grease was saponifiable[2].

Several workers[32,33] have pointed out that the capillary activity of ionic detergents showed an increase in the presence of electrolytes. The same observation was made from a study on nonionic detergents[34] but the initial increase in detergency was followed by a decrease as the salt concentration was increased further. Use of neutral builders such as common salt and Glauber's salt has become more widespread since the advent of neutral scouring with nonionic detergents although it has been reported[10] that with certain nonionic detergents, the addition of neutral electrolytes to the scouring bowls will have little or no effect below 60°C.

The addition of neutral electrolytes to solutions of nonionic detergents has been shown to cause a depression of the cloud point, possibly by dehydration of colloidal micelles[58] or by breakdown of the hydrogen bonds by which the molecules are dissolved in water[51]. The actual amount of depression depends on the nature and the amount of inorganic material added. Such depression of the cloud point indicates that a change in the hydrophile-lipophile balance of the detergent has taken place, which is an important effect since the efficiency of a detergent is largely determined by this balance.

The present study was designed to investigate the effect of the addition of three types of builder to the scouring liquors. Of the builders investigated, two were neutral, viz. sodium chloride and sodium sulphate and one was an alkaline builder, viz. sodium carbonate. The experiment was carried out in two parts, the first to establish the optimum total quantity of builder to be added to the first and second bowls. The same builder was used in both the first and second bowls, and three different detergents (two nonionics and soap) were used. The second part was aimed at establishing the optimum ratios in which the builders should be added to the first and second bowls, on the basis of the optimum total additions obtained in the first part. Combinations of builders were also investigated and the same nonionic detergent was used throughout the second part of the experiment.

7.2 Materials.

Soap, which is an anionic detergent, and two nonionic detergents, Triton N100 and Tergitol NPX, were used in the first series of experiments. The nonionic detergent, Nonidet P40, was used in the second series.

The builders used were soda ash (commercial grade sodium carbonate), Glauber's salt (commercial grade sodium sulphate) and common salt (marine grade sodium chloride).

Two lots of wool were used in the experiments. The first series was carried out on a short belly-wool which yielded 50.7% clean wool and contained 12.6% grease and 8.9% suint. The second lot had an average length of approximately 3 inches and a clean yield of 56.8% and contained 12.4% grease and 8.4% suint. (All calculations are based on dry weights). Each lot of wool was blended separately, put through a fleece-breaker, blended again and rebaled. Lots of 600 lb. raw wool were used in each of the experiments.

7.3 Experimental.

The pilot plant described previously was used in this study. The rakes were set at 11 s.p.m. and the rollers at 6 r.p.m. Rates of feed of 200 and 166 lbs. per hour were used in the first and second parts respectively. The rate of backflow (see Chapter 4) was set at 125% for the first series (short wool) and at 100% for the second in view of the different rates of feed employed. The concentration of total solid matter was approximately 3% after the runs had been completed. Clean water was added to the rinse bowl at a rate of 420 gall. per hour.

The temperatures, which were kept constant for all lots, were as follows:

First bowl	55°C
Second bowl	55°
Third bowl	50°
Fourth bowl	40°
Dryer	45°

The initial charges of detergents used in this study were of the same order as those described in the previous chapter.

In the first series of experiments, only one builder was used in each run, and was added to both the first and second bowls in the ratio of 1 to 1.75. The total amounts of builders used (first and second bowls) per 100 lb. raw wool were 0, 2.75, 5.5 and 11 lb. for each builder with each of the three detergents. (See para. 7.4).

In the second series, the effects of the ratio of builder additions to the first and second bowls and of combinations of builders were investigated. The total amount of builders used was that which was found in the first series to give minimum detergent consumption, viz. approximately 5 lb./100 lb. raw wool. The use of either sulphate or carbonate and of a combination of carbonate and sulphate was investigated in detail. It was assumed that sulphate would have the same type of effect as chloride and the behaviour of chloride as a replacement for sulphate was studied at the points of minimum consumption found for the sulphate. (See para. 7.4).

The builders were added continuously from overhead tanks. Soap solution (1 lb. per 5 litres) and undiluted detergent additions were made continuously as described in Chapters 3 and 5 in order to keep the residual grease content of the scoured wool at approximately 0.6%. The residual grease determinations were carried out on the column-and-tray apparatus at 5 minute intervals.

The pH of the liquors in the first and second bowls was measured at half-hourly intervals using a Metrohm E 280A portable pH meter.

To test the commonly accepted view that the addition of sodium carbonate to the scouring liquors causes discolouration of the wool and that it increases the discolouration of already stained wools[67], a paired comparison experiment was carried out on the four extreme lots from the first series of experiments with Triton N100 scoured under the following four sets of conditions: no builders, 11 lb. sulphate, 11 lb. chloride and 11 lb. carbonate used per 100 lb. raw wool. The paired comparison experiment was designed to indicate any differences between the four lots with regard to colour and handle. An analysis of variance was applied to the data (see e.g. Bliss[68]. In this experiment, the technique of Mosteller[69] was followed in that the preference proportions were transformed into arc sines and not into rankits). Twelve judges, all of whom were familiar with the trade concepts of "colour" and "handle" were used in the experiment.

7.4 Results.

The highest pH, measured after 3 hours, in the first series of experiments was 10.5, when 5.5 or 11 lb. carbonate was used per 100 lb. raw wool. The final pH measurements when chloride, sulphate and no builders were used were very similar and ranged from 7.5 to 8.0.

The detergent consumption in lb./100 lb. raw wool found in the first series for varying builder additions were as in Table 14 and Figs. 15, 16 and 17.

The final pH values recorded in the second series of experiments were of the same order as those in the first series; they varied from 6.8 for no builders and neutral builders to 10.5 in some cases where carbonate was used.

The detergent consumption figures (in lb./100 lb. raw wool) obtained in the second series for varying builder additions are given in Table 15.

TABLE 14

Detergent consumption (in lb./100 lb. raw wool) and residual grease values for different detergents under varying builder additions

Detergent	Builder	Total builders (lb./100 lb. raw wool)	Detergent consumption	Residual Grease (%)
Triton N100	Sulphate	0	1.684	0.67
		2.75	1.512	0.58
		5.5	0.986	0.49
		11.0	1.022	0.53
	Chloride	0	1.684	0.67
		2.75	0.929	0.59
		5.5	0.763	0.61
		11.0	0.669	0.56
	Carbonate	0	1.684	0.67
		2.75	0.534	0.56
		5.5	0.465	0.62
		11.0	0.355	0.56
Tergitol NPX	Sulphate	0	1.340	0.60
		2.75	1.141	0.53
		5.5	1.121	0.58
		11.0	1.123	0.60
	Carbonate	0	1.340	0.60
		2.75	0.634	0.57
		5.5	0.514	0.57
		11.0	0.276	0.58
Soap	Sulphate	0	4.50	0.86
		2.75	3.63	0.80
		5.5	3.10	0.69
		11.0	2.80	0.62
	Chloride	0	4.50	0.86
		2.75	3.30	0.66
		5.5	3.38	0.53
		11.0	3.28	0.64
	Carbonate	0	4.50	0.86
		2.75	1.50	0.60
		5.5	1.25	0.60
		11.0	1.05	0.54

TABLE 15

Consumption of Nonidet P40 (in lb./100 lb. raw wool) for varying builder additions

Builder		Builder ratio	Detergent	Grease
Bowl 1	Bowl 2	Bowl 1:Bowl 2	consumption	(%)
Sulphate	Sulphate	1:4	1.000	0.59
		2:3½	1.311	0.61
		3:3	1.318	0.60
		3½:2	1.325	0.62
		4:1	1.371	0.67
Chloride	Chloride	1:4	0,704	0.58
Carbonate	Carbonate	1:4	0,405	0.49
		2:3½	0.362	0.54
		3:3	0.340	0.53
		3½:2	0,395	0.55
		4:1	0.413	0.60
Carbonate	Sulphate	1:4	0.671	0.49
		2:3½	0.554	0.58
		3:3	0.532	0.56
		3½:2	0.618	0.59
		4:1	0.514	0.53
Carbonate	Salt	2:3½	0.383	0.57

Tables 16 and 17 give the results obtained in the paired comparison experiment on the handle and colour of the lots scoured under conditions of extreme builder additions. The samples, when tested for total alkali [70], gave 47.5, 50, 52 and 102 micromoles/g. conditioned wool for no builder, sulphate, chloride and carbonate treatments respectively.

TABLE 16

Paired comparison experiment for judgement of colour

a) Frequency with which the colour of the sample in the row was preferred to that in the column.

	No builder	Sulphate	Carbonate	Chloride
No builder		2	12	7
Sulphate	10		11	10
Carbonate	0	1		0
Chloride	5	2	12	

b) Preference score of the colour of a particular sample.

No builder	Sulphate	Carbonate	Chloride
7.2	17.5	-29.5	4.8

c) Analysis of variance

	d.f.	S.S.	M.S.	F
Treatments	3	5006	1669	6.8
Error	3	735	245	
Total	6	5741		

TABLE 17

Paired comparison experiment for judgement of handle

a) Frequency with which the handle of a sample in the row was preferred to that in the column.

	No builder	Sulphate	Carbonate	Chloride
No builder		5	9	9
Sulphate	7		7	7
Carbonate	3	5		6
Chloride	3	5	6	

b) Preference scores of the handle of a particular sample.

No builder	Sulphate	Carbonate	Chloride
6.2	3.7	-5	-5

c) Analysis of variance

	d.f.	S.S.	M.S.	F
Treatments	3	412	137	3.6
Error	3	113	38	
Total	6	525		

7.5 Discussion.

The effect of builder additions on soap consumption can be seen from Fig. 15. There is little difference between the

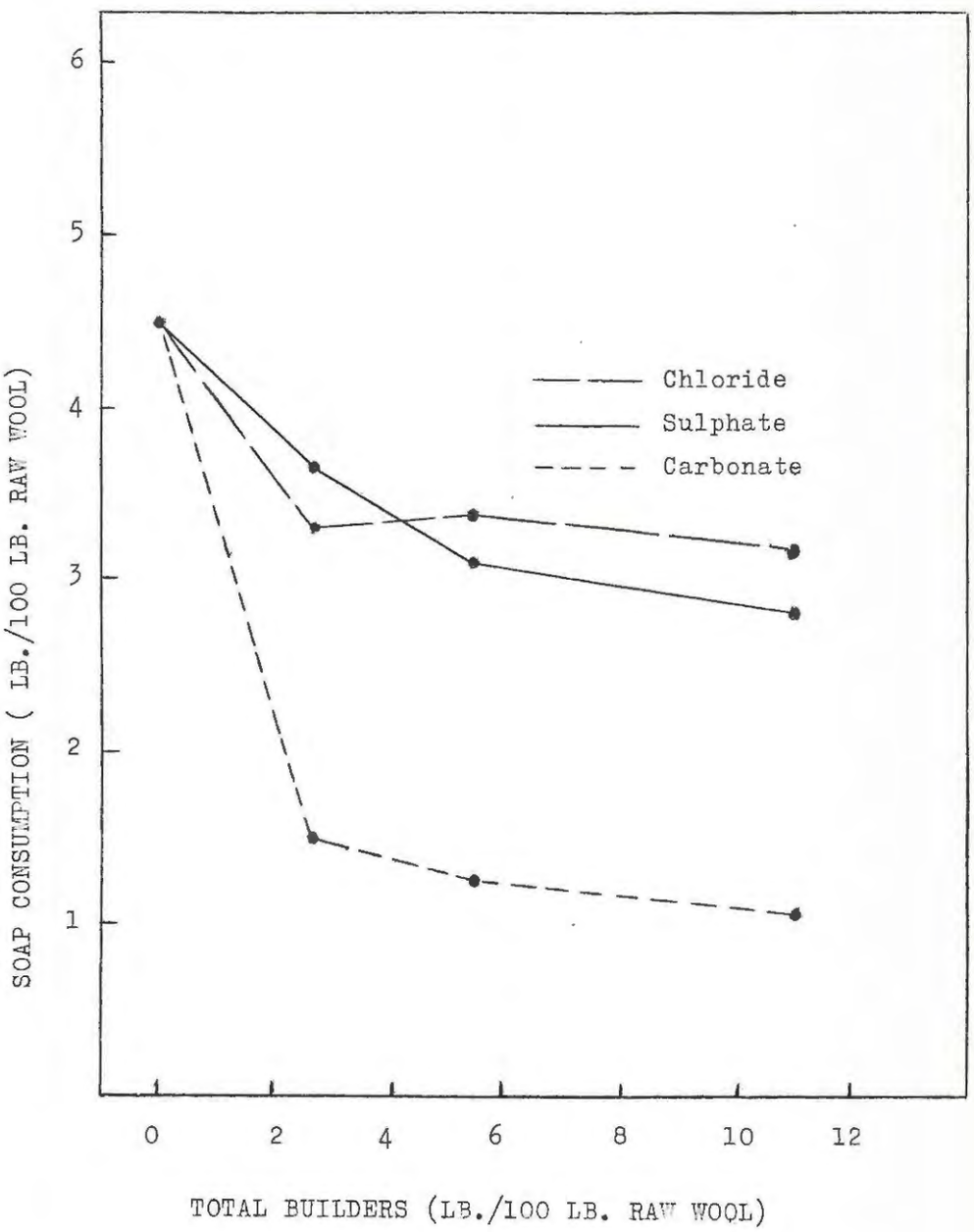


Fig. 15. Effect of the addition of detergency builders on the consumption of soap.

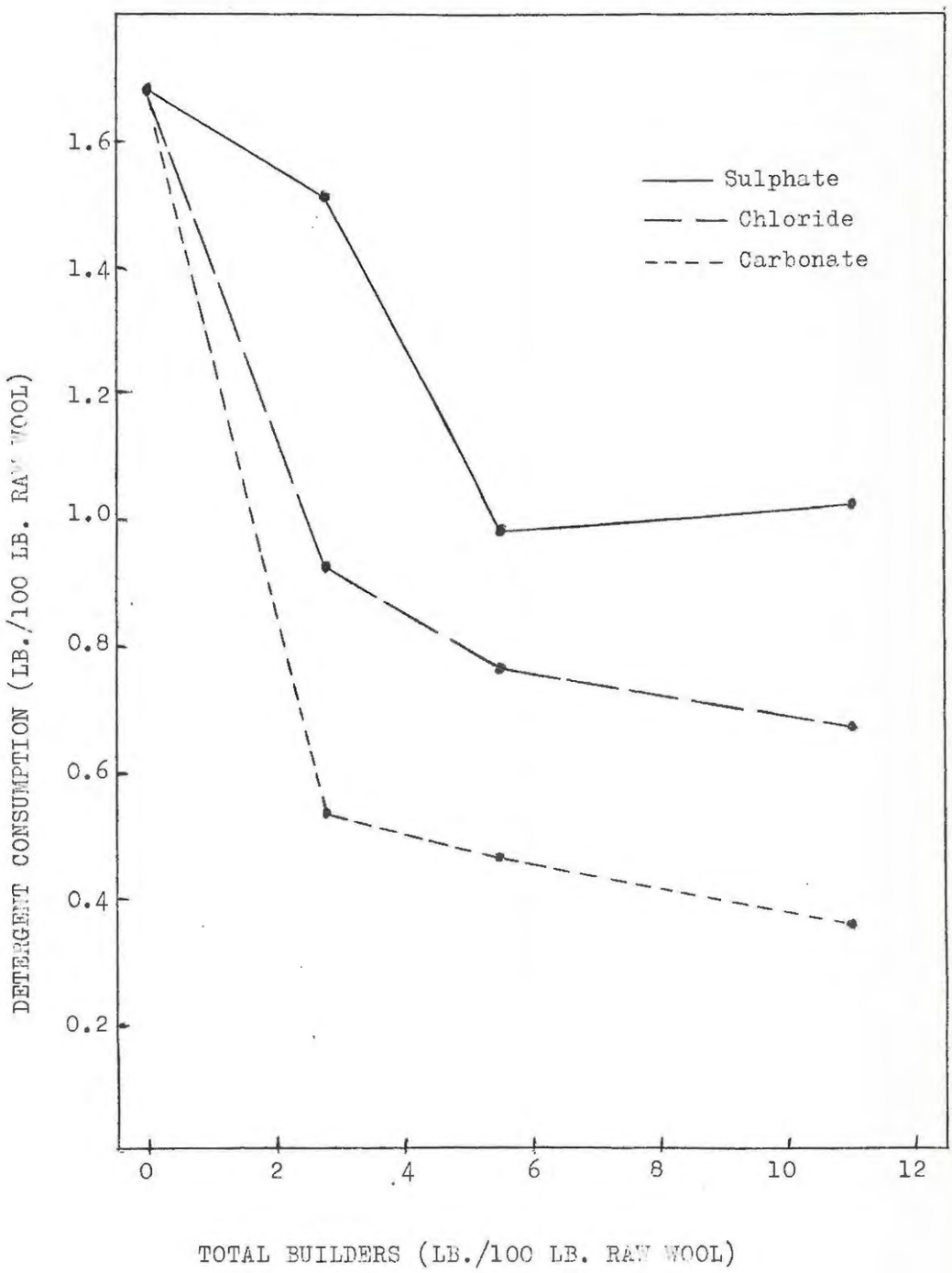


Fig. 16. Effect of the addition of detergency builders on the consumption of Triton N100.

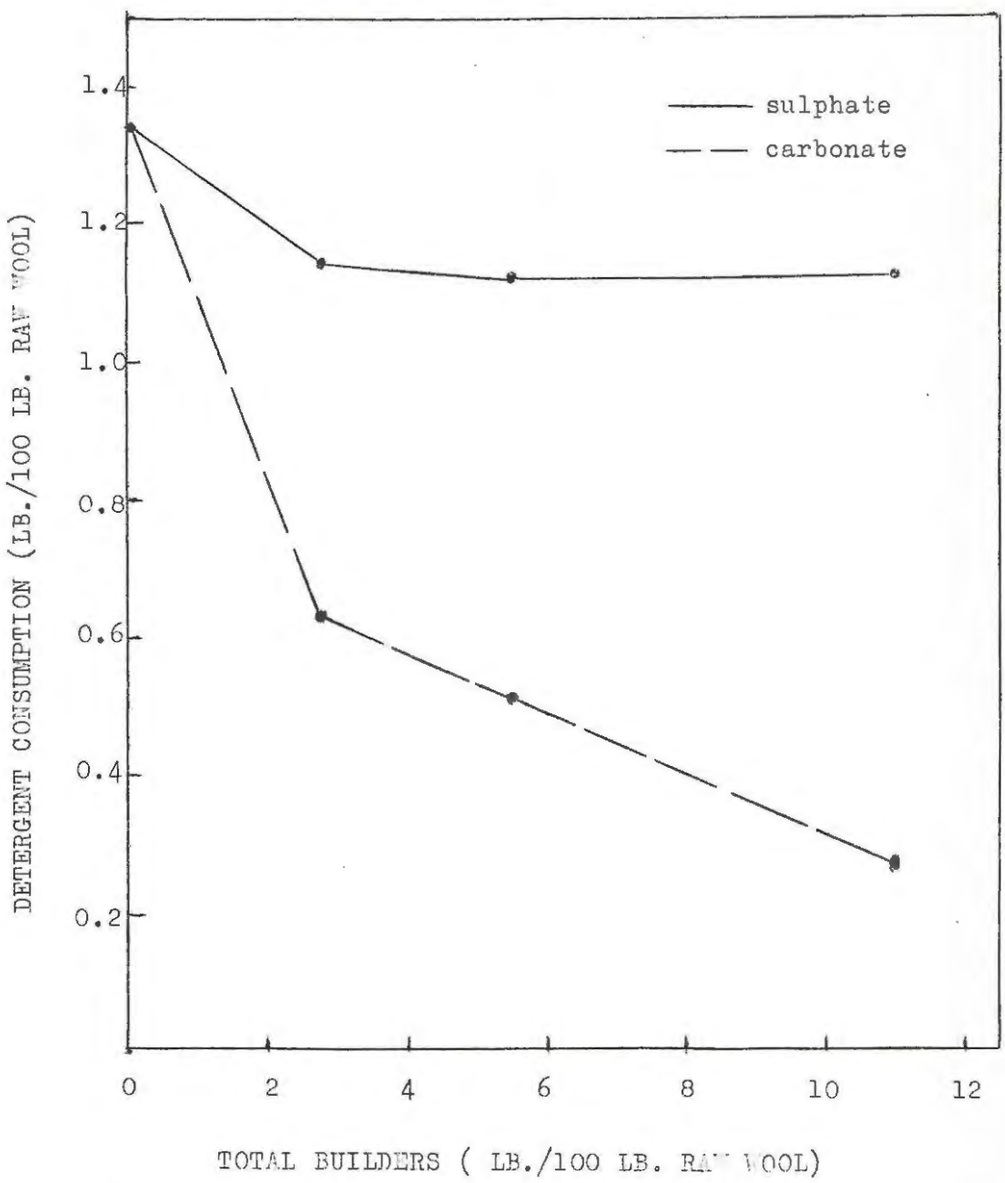


Fig. 17. Effect of the addition of detergency builders on the consumption of Tergitol NPX.

effects of sulphate and chloride, whereas addition of carbonate causes a considerable decrease in detergent consumption.
The effect of builder additions on the consumption of the two nonionic detergents may be seen from Figs. 16 and 17. In the case of Triton N100, the order of effectiveness was: carbonate, chloride and sulphate. For Tergitol NPX the effect of additions of sulphate and carbonate was investigated and found to be similar to that obtained for Triton N100. In view of the similarity found for the other builders, it was assumed that chloride would in this case also be of intermediate effectiveness between carbonate and sulphate.

These results can be related to the theories of Palmer[31] and Cassie and Palmer[71] who suggested that in the presence of salts, the potential energy of detergent ions in solution is decreased by the concentration around them of ions of opposite sign (Debye - Hückel effect). The potential energy of detergent ions at the surface is decreased to an even greater extent. The amount of detergent in the surface in equilibrium with a given bulk concentration depends on the difference in potential energy of a detergent ion in the two zones. A greater lowering of the potential energy of detergent ions in the surface will, therefore, give greater surface pressures and probably also greater detergence. In terms of this theory, it is expected that only ions of sign opposite to the detergent ions will have an appreciable effect. From Fig. 15 for soap, which is an anionic detergent, it will be seen that there is no marked difference in changing the anion from chloride to sulphate while the cation remains the same (Na^+ in this case) which is in direct agreement with the theory. It will be seen that carbonate additions cause a further

improvement in detergency, which suggests that a different mechanism is operating in this case. Sodium carbonate is an alkaline builder which increases the pH of the scouring liquors. The final pH values recorded at the different levels of carbonate additions were: 0% carbonate, 7.7; 2.75% carbonate, 9.8; 5.5% carbonate, 10.3 and 11% carbonate, 10.4. These figures show an increase in a manner resembling the decrease in detergent consumption in Fig. 15. It has been suggested[72] that an increase in pH of detergent solutions will give a greater proportion of soap anions in the surfaces, again giving greater surface pressures and presumably also increasing detergence, which is borne out by the results presented in Fig. 15.

The rather marked effect of builder additions on the non-ionic detergent consumption shown in Figs. 16 and 17 seemed anomalous from the point of view of the theory of Cassie and Palmer[71] since these detergents do not ionise in water. There is considerable evidence, from the similarity of their behaviour to that of cationic detergents in aqueous solutions, that nonionic detergents should be regarded as oxonium compounds[73]. In view of this fact and the above theory[71], one would expect that a change in the type of anion of the builder used would cause differences in detergence. This effect was, in fact, observed eg. in Figs. 16 and 17 where there is a considerable difference in detergent consumption between sulphate, chloride and carbonate when the cation (Na^+) remains the same in all cases. The exact mechanism of the changes is not clear, since the magnitude of the effects does not seem to be directly related to molecular size or molecular concentration of builders in the scouring liquors when all three builders are considered. For chloride and sulphate alone, the picture is

somewhat clearer, and it is possible that a different mechanism, in which the dominant effect is that of pH on the distribution of detergent ions in the system, operates in the case of carbonate.

From Figs. 15, 16 and 17 it will be seen that in all cases there is a marked decrease in detergent consumption from zero builders to 2.75% additions, a smaller decrease from 2.75% to 5.5% and an almost negligible decrease from 5.5% to 11.0%. These results are in agreement with the observations of Palmer[31] and McLaren[34] who found an increase in detergency for additions of electrolyte up to a certain concentration level and a decrease when this level was exceeded.

For the second series of experiments, the total additions of builders varied from 5 to 6 lb./100 lb. raw wool. The weights used were chosen in order to simplify the practical operation of the plant and it was thought that the small differences would not cause significant changes in detergent consumption since the experiments were carried out in the flattest region of the detergent consumption - builder concentration curves (see Figs. 15, 16 and 17).

It will be seen from Table 15 that the effectiveness of the different builders are in the same order as before: carbonate, chloride and sulphate. Also, when the neutral builders were combined with carbonate, chloride was found more efficient than sulphate and the carbonate caused marked decreases in detergent consumption in both cases.

The ratios in which the sulphate was added to the first and second bowls did not make much difference to the detergent consumption in most cases, although there was a reasonable decrease

at a ratio of 1:4. This was taken to be the optimum ratio for the addition of neutral electrolytes and the detergent consumption figure for chloride was also obtained under these conditions. When carbonate was used in the first bowl and sulphate in the second, the minimum detergent consumption was at a ratio of 4:1, but it was decided to use the ratio 2:3½ as optimum even though the detergent consumption at this point was somewhat higher in order to avoid the potential discolouring effect of high concentrations of carbonate. Once again, it seemed that a different mechanism was operating in the case of carbonate, in that the small differences in total additions largely outweighed any effects due to different ratios of additions.

Tables 16 and 17 give the results obtained in the paired comparison experiments and the analyses of variance. It will be seen that the effect of colour is significant at a 10% level, whereas the handle results are not significant. It should be pointed out, however, that in view of the comparatively small number of observations and degrees of freedom, only clear differences appear as significant. It can therefore be said that the colour of the sample from the carbonate scour was least acceptable. The handle, however, cannot be judged similar in all cases, since there might have been small differences which did not appear to be significant in the analysis. It must be stressed that this experiment was carried out on the extreme lots (conditions which would not normally be encountered in actual practice) and was intended to indicate more clearly those differences which may exist under milder conditions by exaggerating them. It is clear that the presence of excessive amounts of sodium carbonate has a detrimental effect on the colour of scoured wool.

7.6 Conclusion.

The order of efficiency of the builders used for nonionic detergents was found to be: sodium carbonate, sodium chloride and sodium sulphate. For soap, sodium carbonate was by far the most efficient builder, whereas sodium sulphate and sodium chloride had similar effects.

Detergent consumption was found to decrease sharply on increasing additions of builders in the lower concentration ranges. The effect became considerably less marked in the higher ranges.

When the total additions were kept constant the ratio of addition of builders to the first and second bowls did not appear to have any marked influence on detergent consumption.

From a paired comparison experiment conducted on samples scoured under extreme conditions of builder additions it was concluded that the use of excessive amounts of sodium carbonate had a significant discolouring effect on the scoured wool.

SECTION II : LABORATORY STUDY

8. DETERMINATION OF NONIONIC DETERGENTS IN AQUEOUS SOLUTIONS.

8.1 INTRODUCTION

8.1.1 Composition of nonionic detergents.

The majority of nonionic textile chemicals are prepared by the reaction of ethylene oxide with materials such as alkylphenols, alcohols, acids, mercaptans, amides and amines which contain reactive hydrogen atoms. (See Table 18) The water solubility of ethylene oxide condensation products can be altered by increasing the number of ethylene oxide units. Other nonionic detergents are the fatty acid esters of sorbitan (a tetrahydroxy alcohol) and of sorbitol (a hexahydroxy alcohol)[74].

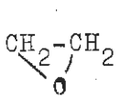
A different type of nonionic based on alcohols comprises the ethylene oxide derivatives of polypropylene glycol. Although propylene glycol itself is water-soluble, polypropylene glycols with molecular weights higher than about 900 are insoluble in water and can serve as a hydrophobic base for nonionics[75].

It is obvious that it is possible to make an almost infinite number of nonionic surfactants when the number of starting materials is considered and in view of the fact that it is a relatively simple process to vary the molecular ratio (denoted by n) of ethylene oxide to hydrophobic reactant.

Nonionic detergents can be prepared in very pure form, the only impurities being small amounts of catalyst, as distinct from anionic detergents which normally contain inorganic salts as impurities. It has been shown[62] that when nonylphenol reacts with ethylene oxide, the weight per cent distribution of fractions containing the various molecular ratios of combined ethylene oxide follows Poisson's distribution formula.

TABLE 18

Derivation of nonionic surfactants from ethylene oxide[74]

Ethylene Oxide		Hydrophobe		Product
n 	+	R-  -OH (phenol)	⟶	R-  -$(OCH_2CH_2)_nOH$
	+	ROH (alcohol)	⟶	$R-(OCH_2CH_2)_nOH$
	+	RCOOH (acid)	⟶	$R-C(=O)-(OCH_2CH_2)_nOH$
	+	$RCONH_2$ (amide)	⟶	$R-C(=O)-N(-(CH_2CH_2O)_aH)-(CH_2CH_2O)_bH$
	+	RNH_2 (amine)	⟶	$R-N(-(CH_2CH_2O)_aH)-(CH_2CH_2O)_bH$

In the latter two cases n = a+b.

8.1.2 Qualitative tests.

The majority of the qualitative tests available for nonionic detergents are based on

a) The phenomenon of "clouding"[51], i.e. the development of turbidity on heating,

b) Precipitation of the oxonium salt of the polyoxyethylene compound by large anions such as cobaltothiocyanate, phosphomolybdate, etc. (See under quantitative analysis).

The latter test suffers from the disadvantage that it is essentially a modification of the generally used precipitation test for cationic surfactants by means of a large anion[76,77], and is therefore given by all cationic surfactants with or without the polyethylene oxide group in the molecule. This similarity of nonionics to cationics was one of the reasons which led

Wurzschmitt[73] to believe that polyethylene oxide derivatives should be regarded as oxonium compounds.

It was found by Rosen[78] that all types of compounds containing the polyoxyethylene group may be detected by pyrolysis in 85% phosphoric acid and leading the volatile products into an aqueous solution of sodium nitroprusside containing a water-soluble secondary amine such as diethanolamine. Decomposition of the polyethylene oxide group results in the formation of acetaldehyde which gives a blue colour with sodium nitroprusside and the secondary amine[79].

$$-(OCH_2CH_2)_{\overline{n}} \xrightarrow[\text{heat}]{H^+} xCH_3CHO + -(CH_2CH_2O)_{\overline{(n-x)}}$$

$$CH_3CHO + \left[Fe(CN)_5NO\right]^{2-} + 2R_2NH \longrightarrow$$

$$\left[Fe(CN)_5 \begin{matrix} NNR_2 \\ \| \\ CHCHO \end{matrix}\right]^{3-} + R_2NH_2^+ + H_2O$$

(blue)

Under similar conditions of test the polyoxypropylene group decomposes to give propionaldehyde and its polymers which produce orange colours with sodium nitroprusside and diethanolamine.

$$-(OCH_2\underset{\underset{CH_3}{|}}{CH})_{\overline{n}} \xrightarrow[\text{heat}]{H^+} xCH_3CH_2CHO + (CH_3CH_2CHO)_y + -(OCH_2\underset{\underset{CH_3}{|}}{CH})_{\overline{n-(x+y)}}$$

$$CH_3CH_2CHO + \left[Fe(CN)_5NO\right]^{2-} + 2R_2NH \longrightarrow$$

$$\left[Fe(CN)_5 \begin{matrix} NNR_2 \\ \| \\ CH_3CCHO \end{matrix}\right]^{3-} + R_2NH_2^+ + H_2O$$

(red-orange)

The only types of compound which give this test without containing the polyoxyethylene group are the glycerides. This is due to the fact that glycerides form acrolein under the conditions of the test which gives a blue colour as does acetaldehyde.

8.1.3 Quantitative analysis.

The quantitative methods for the estimation of nonionic detergents may be broadly classified under three headings:- gravimetric, volumetric and colorimetric or absorptiometric procedures. Again, the majority of these methods are based on the precipitation of the oxonium salts of the polyoxyethylene compound by a large anion, which is also a method of determining cationic surfactants and therefore not specific[76,77].

Shaffer and Critchfield[80] observed that high molecular weight polyethylene glycols gave a precipitate with silicotungstic acid in the presence of $BaCl_2$ and HCl and developed a gravimetric procedure based on this principle. They found, however, that protein material interfered with the estimation by also forming a precipitate with silicotungstic acid. The gravimetric method of Oliver and Preston[81] is based on a precipitation reaction with phosphomolybdic acid and $BaCl_2$ in HCl medium. A disadvantage of this method lies in the fact that the precipitated complex has to be left overnight before it can be filtered. Barber, Chinnick and Lincoln[82] have described a similar method using phosphotungstic acid which has the advantage that the precipitate may be filtered within 2 - 3 hours after precipitation. These authors have claimed higher accuracy than with phosphomolybdic acid. They also reported that silicotungstic acid gave gummy precipitates which were difficult to filter although precipitation with silicotungstic acid has been declared useful[83] for nonionics

having six or more ethylene oxide units in the hydrophilic polymer. The lower ethylene oxide adducts yield complexes which appear to be too soluble in aqueous acid. Haakh, von Candié and Möbus[84] precipitated ethylene oxide products with a resorcinol-glucose condensation compound and determined the resultant complex gravimetrically.

A volumetric method has been proposed by Schönfeldt[85,86] who precipitated ethylene oxide adducts with an excess of potassium ferrocyanide and titrated the unused reagent with $ZnSO_4$ solution. The results obtained agreed to within approximately 5%. According to Seher[87], nonionics can also be determined by precipitation with sodium tetraphenyl-boron. The precipitate is made into a suspension with NN-dimethylformamide and sodium acetate and an excess of mercurous nitrate added. The excess is determined by titration with NH_4CNS solution. Cationics interfere in that they also give a precipitate with sodium tetraphenyl-boron. Coppini and Cameroni[88] determined nonionic compounds by precipitation with potassium ferrocyanide and determination of the excess ferrocyanide with $FeCl_3$.

Colorimetric methods include that of Shaffer and Critchfield[80] who precipitated the glycol with phosphomolybdic acid and determined the molybdenum content of the precipitate. A similar method is due to Stevenson[89] who dissolved the precipitate in concentrated H_2SO_4 and measured the resultant violet colour photometrically at 520 mμ. The violet colour was found to be specific for non-ionic detergents. Stevenson also described a modification to this method for use when the presence of H_2SO_4 in the colorimeter tube is undesirable. This is essentially an adaptation of the method of Snell and Snell[90] for the determination of molybenum

by thiocyanate coloration in the presence of stannous chloride. The coloured complex formed has an absorption peak at 470 mμ. Amounts down to 1 p.p.m. can be estimated, the latter method being the more accurate. MacAllister and Lisk[91] determined polyoxyethylene stearate in dilute solution by the formation of a complex with the amylose fraction of potato starch, the amylose not involved in the complex being free to form an amylose-iodine complex which was estimated colorimetrically. This method can, however, only be used at concentrations down to 0.05%, which is virtually the upper limit of concentration used in scouring.

A UV-spectrophotometric method has been reported by Griffith[92]. The optical density of a solution of a nonionic detergent was measured at 278 mμ (the peak presumably being due to the aromatic ring) and a standard curve for optical density - concentration plotted. Concentrations down to 0.005% w/v Triton X100 could be determined with an accuracy of better than 1%. A different spectrophotometric method was reported by Brown and Hayes[93] who based their procedure on the qualitative test of van der Hoeve[94] with ammonium cobaltothiocyanate. An ethylene oxide derivative forms a blue precipitate which is extracted into chloroform to give a blue solution, the optical density of which is measured at either 318.5 or 620 mμ. It was found that polyethylene glycol monoleate could be determined accurately to within 0.0094 g./litre. Heatley and Page[95] precipitated the nonionic according to the method of Oliver and Preston[81], washed the precipitate with NH_4Cl solution and re-dissolved it in a solvent mixture consisting of 5N HCl and 2-methoxyethanol (1:4 by volume) for ultra-violet spectrometry at 310 mμ against a blank of the solvent mixture alone. According to Pitter[96], nonionics can also

be determined by dissolving in concentrated H_2SO_4 the precipitate formed with phosphotungstic acid. The solution is mixed with a 5% w/v hydroquinone solution in 98% H_2SO_4, and the optical density of the resulting red solution measured at 500 mμ. Reproducibility at 3 mg. content of nonionic is in the region of 3%. Results are poorly reproducible with surfactants of low ethylene oxide content. Anions which precipitate with $BaCl_2$ in acid medium interfere with the determination, as would protein material. It also follows that any substances which absorb in the wavelength regions mentioned will interfere with the determinations.

The principal disadvantages of the above methods lie in the fact that they are tedious, often not capable of high accuracy and unsuitable for use as routine methods by untrained operatives. It has been shown by Weatherburn and Bayley[54] and by Le Compte and Creely[55] that the amount of sorption of nonionics by wool is very small and it is imperative that any method used in this kind of work should be capable of detecting very small changes in concentration.

8.1.4 Separation of interfering substances.

Several authors have mentioned the fact that cationic detergents interfere with the precipitation of nonionics by a large anion[78,82,97]. It was suggested by Barber et al[82] that cations could be removed quantitatively from solution by using a cation exchange resin, leaving the nonionic to be analysed separately. It has been reported by Green, Harker and Howitt[98] that an anion exchanger will remove cetyltrimethyl-ammonium bromide, an anionic agent, from an aqueous solution. The same general observation was made by Rosen[99]. Hobson and Hartley[100] found that the presence of substantial amounts of fatty matter or dyes

interfered with the methods of Oliver and Preston[81] and that of Brown and Hayes[93]. They reported that fatty matter could be separated from the nonionic by passing an aqueous ethanolic dispersion of the mixture through an alumina column when the fatty matter is retained whereas the nonionic agent passes through the column. Gatewood and Graham[101] have indicated that they had obtained good separations between nonionic, cationic and anionic detergents using the methods of Rosen[99] and of Hobson and Hartley[100]. Nonionics may be extracted from mixtures with soap by the method of Huffins[102] which is based on the fact that the nonionic agents are soluble in cold dioxane.

8.2 METHODS INVESTIGATED

8.2.1 Phosphomolybdic acid method.

Introduction:

Of the gravimetric methods, that of Oliver and Preston[81] and of Barber et al[82] seemed to offer most scope for application in the present study. The latter method showed most promise in view of the fact that the precipitate could be filtered more rapidly and also because it was found that the precipitate from the phosphotungstic acid method weighed almost twice as much as the precipitate obtained from the phosphomolybdic acid determination. The accuracy of the methods was investigated. The effect of the presence of protein material on the phosphotungstic acid method was also determined.

Reagents used:

a) Detergent solutions of known concentrations made up in distilled water.

b) HCl solution, 1 volume conc. HCl dissolved in 4 volumes distilled water.

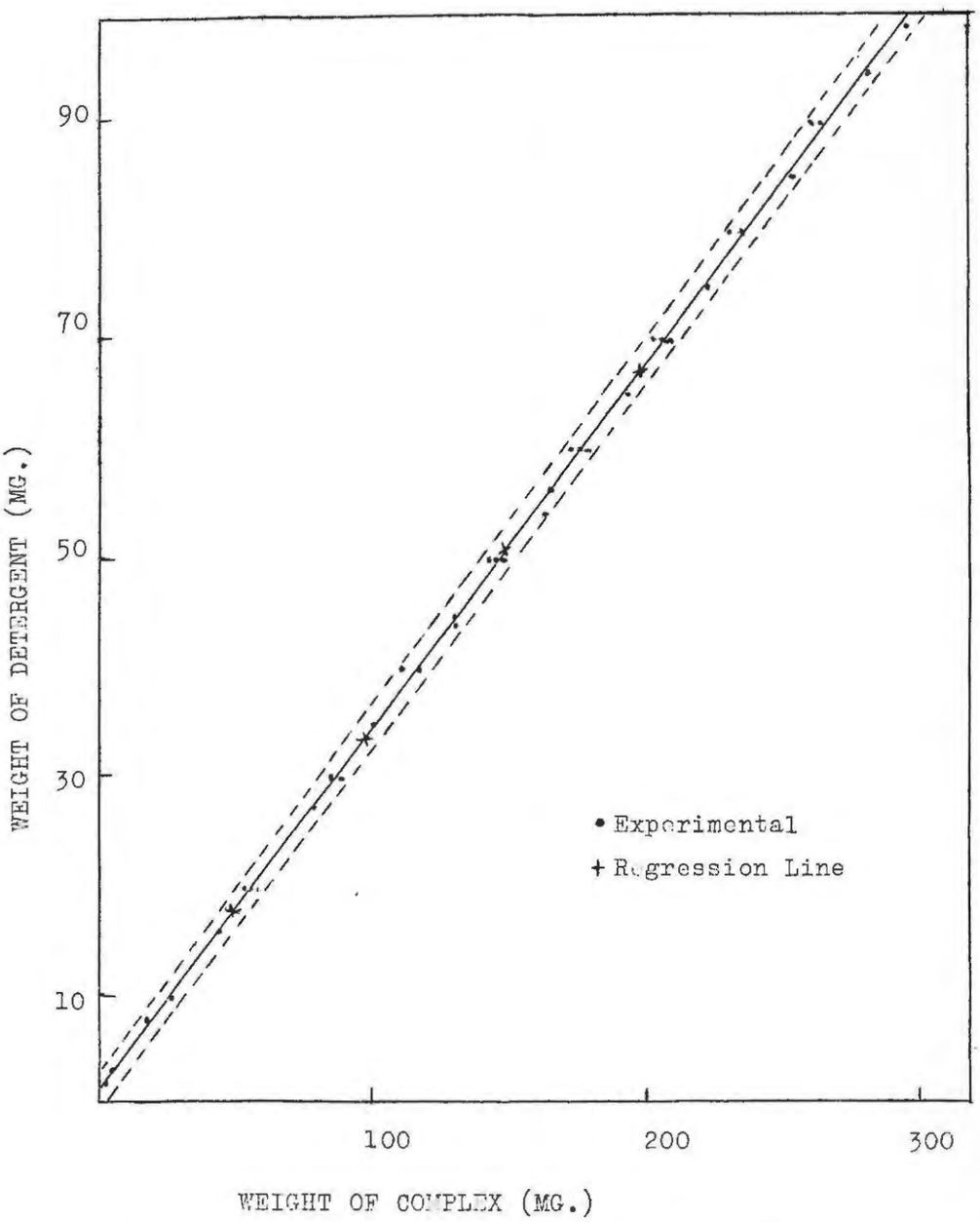


Fig. 18. Calibration curve for Linsapol NX using phosphomolybdic acid as precipitant, showing the 95% confidence limits for the predicted amount of detergent present.

c) 10% $BaCl_2 .2H_2O$ (analytical grade) solution in distilled water.

d) Phosphomolybdic acid (C.P.), $H_3PO_4.12MoO_3.24H_2O$, 10% in distilled water.

Experimental:

An aliquot of the solution containing a known amount of nonionic detergent (not more than 100 mg.) was pipetted into a 250 ml. beaker to which was added 5 ml. each of HCl, $BaCl_2$ and phosphomolybdic acid solutions in this order, and the contents diluted to 150 ml. with distilled water. The solution was heated to the boil to flocculate the yellowish-green precipitate. The beaker was then covered with a watch glass and allowed to stand overnight (18 hours).

The precipitate was filtered in a tared Gooch crucible through an asbestos mat, washed with at least 100 ml. distilled water and dried to constant weight at 105°C.

Results:

The above procedure establishes the ratio of the weight of complex to the weight of the particular detergent preparation under test. On plotting the weight of complex against the weight of detergent a rectilinear graph is obtained (see Figs. 18 and 19) which is used as a calibration curve for the particular detergent. Solutions of the same detergent of unknown concentration can now be analysed by the above procedure and the results interpreted with the aid of the calibration graph.

The method was at first applied to Lissapol NX, with the results shown in Table 19 and Fig. 18. Several duplicates were included to estimate the accuracy and precision of the method.

TABLE 19

Weights of complex found for known weights of Lissapol NX.

mg. detergent	mg. complex
2.0	5.0
4.0	8.5
8.0	21.0
10.0	28.9
15.0	41.7
20.0	54.9, 56.9, 53.2
25.0	72.1
30.0	86.3, 87.6
35.0	101.4
40.0	109.6, 117.2
44.0	130.3
45.0	130.0
50.0	147.5, 142.9, 145.0
51.0	150.5
54.0	162.1
56.0	165.6
60.0	176.0, 174.3, 179.9
65.0	195.8
70.0	207.2, 202.8, 206.5
75.0	224.5
80.0	236.5, 232.6
85.0	254.5
90.0	260.7
95.0	284.0
100.0	298.5

A linear model was postulated[103] and calculated from Table 19 for the case of Lissapol NX:

$$y = 0.3331x + 1.1997$$

Further, the standard error of b, (the regression coefficient), the residual standard deviation (S.D.) and the correlation coefficient[104, 105] for the line was calculated and found to be 0.0105, 0.8842 and 0.9995, respectively. The 95% confidence limits[106] for the predicted amount of detergent present was calculated and are shown in Fig. 18 together with the regression line for the determination of Lissapol NX. It will be seen that an extremely good correlation exists between

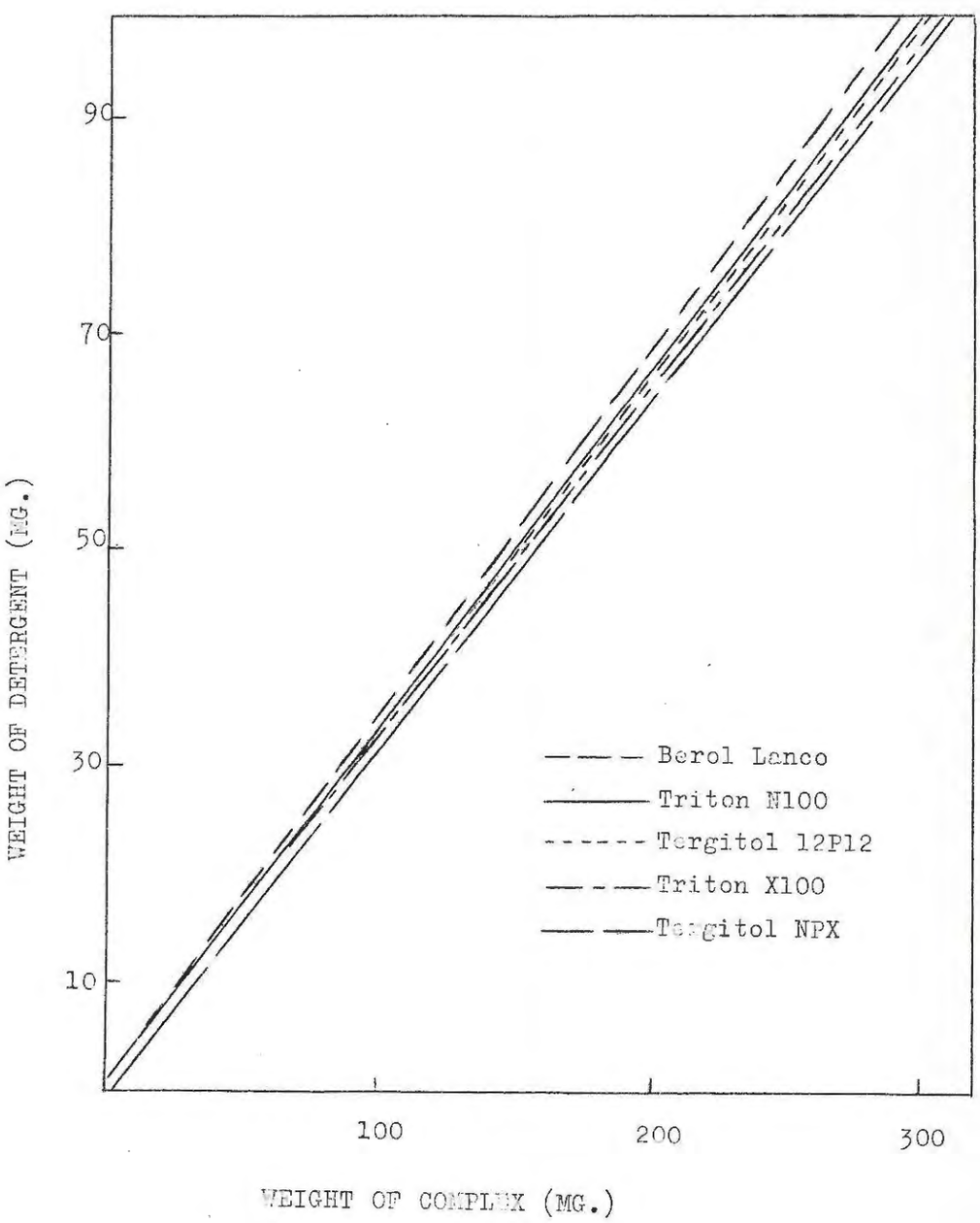


Fig. 19. Calibration curves for various nonionic detergents using phosphomolybdic acid as precipitant.

the two factors and that there is very little spread of points about the estimated line.

On further investigation the method was found to be applicable to a large variety of nonionic detergents as indicated in Table 20 and Fig. 19. It will be seen from the calculations that the same degree of accuracy is maintained in all cases and that the slopes of the lines are of the same order.

TABLE 20

Equations of the phosphomolybdic acid calibration curves for various detergents where y represents the weight of detergent (in mg.) and x the weight of complex (in mg.)

Detergent	Regression Equation	S.E. of b	Residual S.D.	Correlation coefficient
Lissapol NX	y = 0.3331x + 1.1997	0.0105	0.8842	0.9995
Tergitol NPX	y = 0.3219x - 0.5149	0.0045	0.3834	0.9999
Tergitol 12P12	y = 0.3308x + 0.0640	0.0081	0.7884	0.9997
Berol Lanco	y = 0.3430x + 0.4098	0.0056	0.4993	0.9998
Triton X100	y = 0.3220x + 0.9012	0.0044	0.1691	1.0000
Triton N100	y = 0.3309x + 0.5488	0.0015	0.2728	1.0000

Discussion:

It will be seen from the above that this method is highly satisfactory from the point of view of accuracy. The method does, however, suffer from a number of distinct disadvantages. It is time-consuming in that the precipitate has to be left overnight before it can be filtered successfully. If the method were to be applied to scouring liquors as a method of concentration control, it would have to be considerably quicker. Furthermore, sulphates interfere with the precipitation and have to be removed first, and it has been shown that protein degradation material will also interfere, as would wool grease[3]. Where neutral scouring with

nonionic detergents is practised, one of the commonly used detergent builders is Glauber's salt (sodium sulphate), which would thus interfere with the determination. It is also likely that scouring liquors would contain a certain amount of protein degradation material from the action of the hot alkaline solutions on the weathered tips of the fibres[8], and most certainly a fair amount of woolgrease.

It seems that there is very little hope of modifying the method suitably in order to apply it successfully to the control of concentration in scouring liquors. It is, however, admirably suited to the estimation of nonionic detergents in pure aqueous solutions.

8.2.2 Phosphotungstic acid method.

Reagents required:

a) Detergent solutions of known concentration, made up in distilled water

b) HCl acid solution, 1 volume HCl dissolved in 4 volumes distilled water

c) 10% $BaCl_2.2H_2O$ (analytical reagent) solution in distilled water

d) Phosphotungstic acid (C.P.) $H_3PO_4.12WO_3.24H_2O$ 10% solution in distilled water.

Experimental:

To the sample of nonionic detergent (containing not more than 100 mg. detergent) in 200 ml. water 10 ml. HCl solution was added, followed by 10 ml. $BaCl_2$ solution. The mixture was brought to the boil and 10 ml. phosphotungstic acid solution added. The solution was boiled for a further 2 minutes until the precipitate had coagulated and left for

two hours before filtering in a tared Gooch cruicible through an asbestos mat. The precipitate was washed with a minimum of 100 ml. distilled water and dried to constant weight at 105°C.

The interference from protein degradation products on the method when applied to Tergitol NPX was measured as follows: a quantity of 500 ml. of "NaOH extract" was made according to the method of Blackburn[107]. The solution obtained was centrifuged to remove solid matter. After centrifugation, the solution was still somewhat cloudy and to ensure that the matter which remained in suspension did not "mask" the results, the solution was filtered through a Gooch crucible similar to the ones used in filtering the complex precipitate. The filtrate was made up to 500 ml., a 5 ml. aliquot from this solution added to the detergent solutions and the amount of nonionic detergent determined as before.

Results:

As in the phosphomolybdic acid method this procedure establishes the ratio of the weight of complex formed to the weight of detergent present for a given detergent. When plotted, the results give a rectilinear graph which may be used to estimate the concentration of the specific nonionic detergent in unknown solutions.

The method was again found to be applicable to several types of nonionic detergents as shown in Table 21 and Fig. 20.

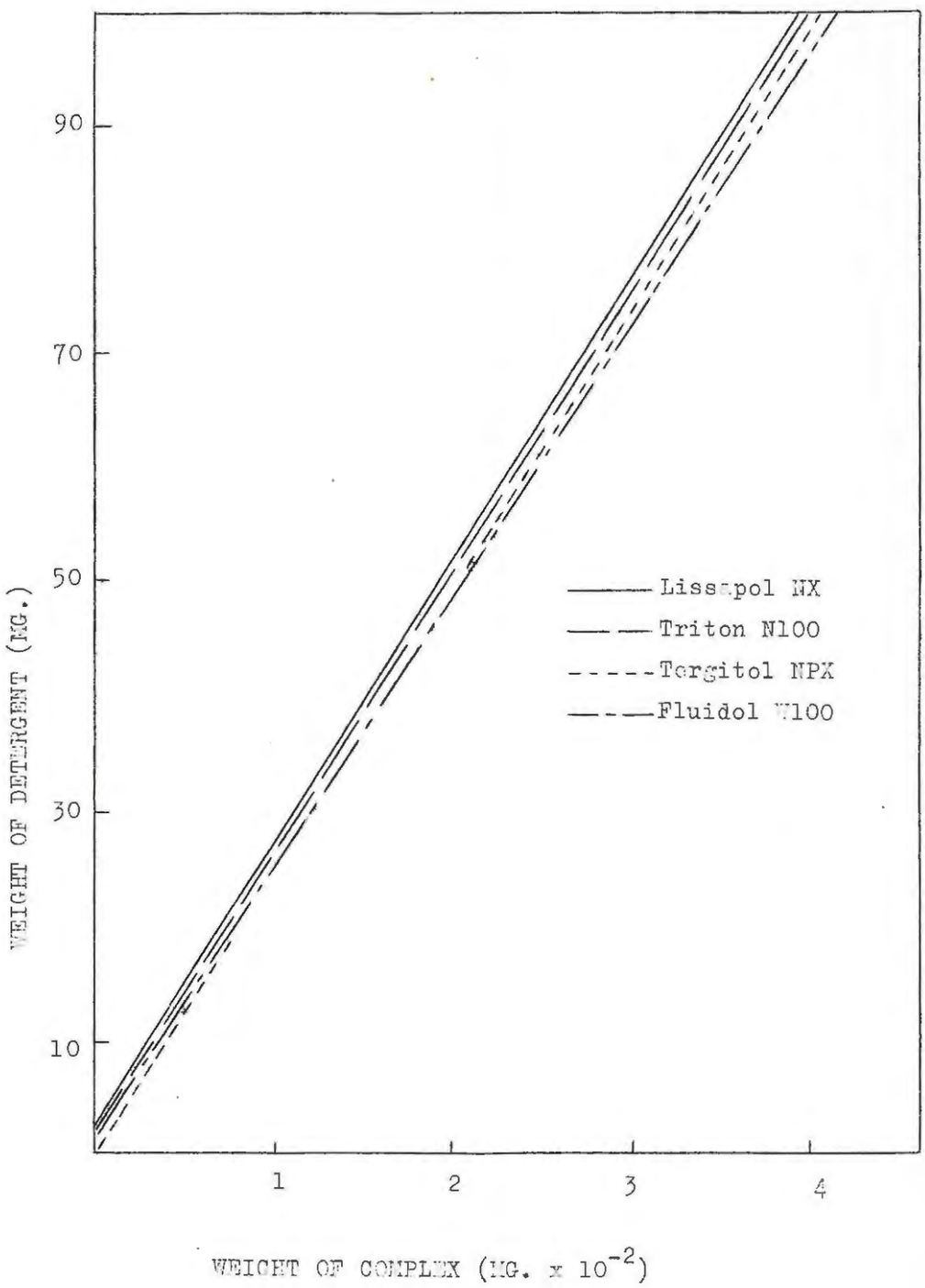


Fig. 20. Calibration curves for various nonionic detergents using phosphotungstic acid as precipitant.

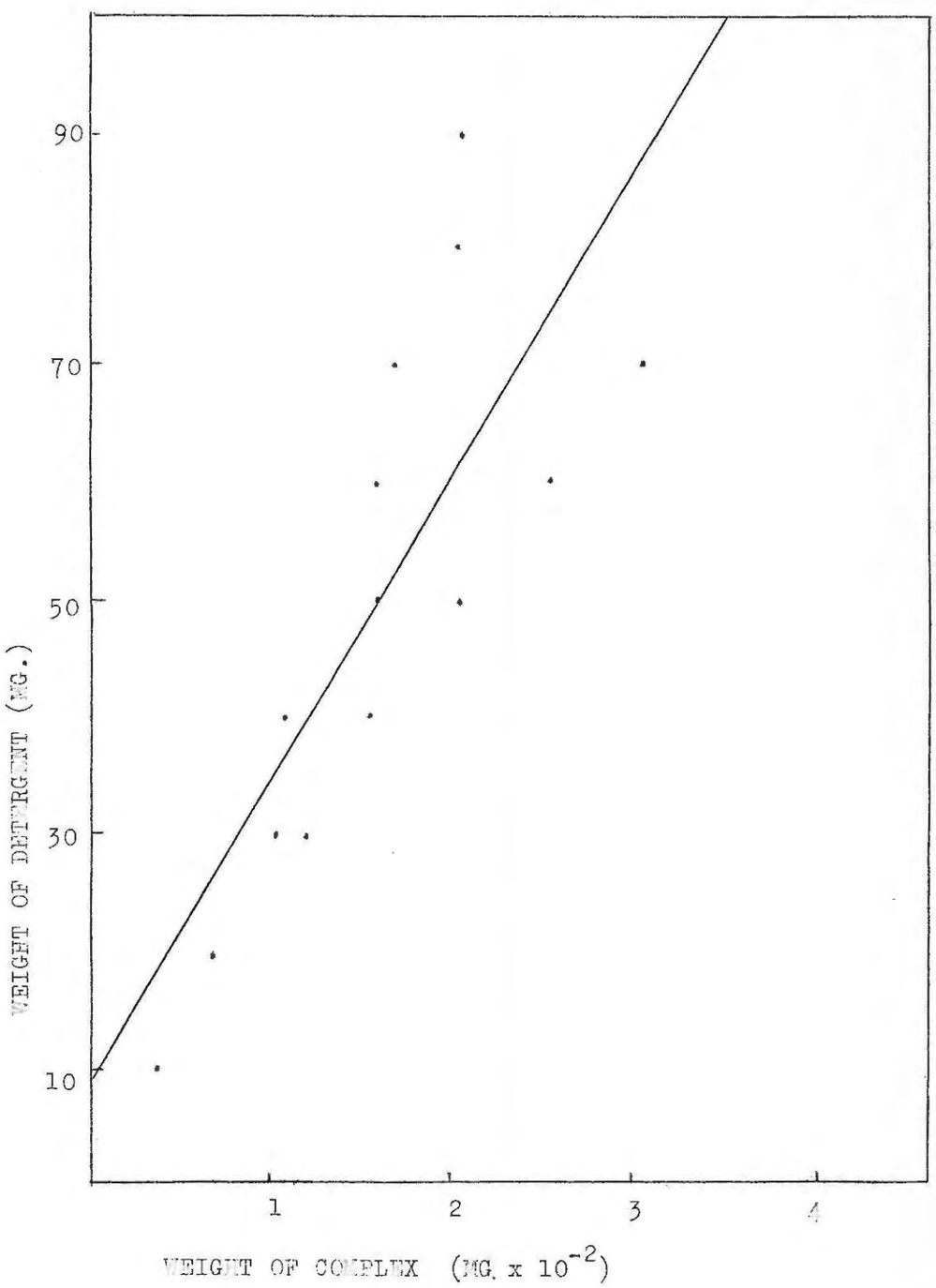


Fig. 21. Calibration curve for Tergitol 12P9 using phosphotungstic acid as precipitant.

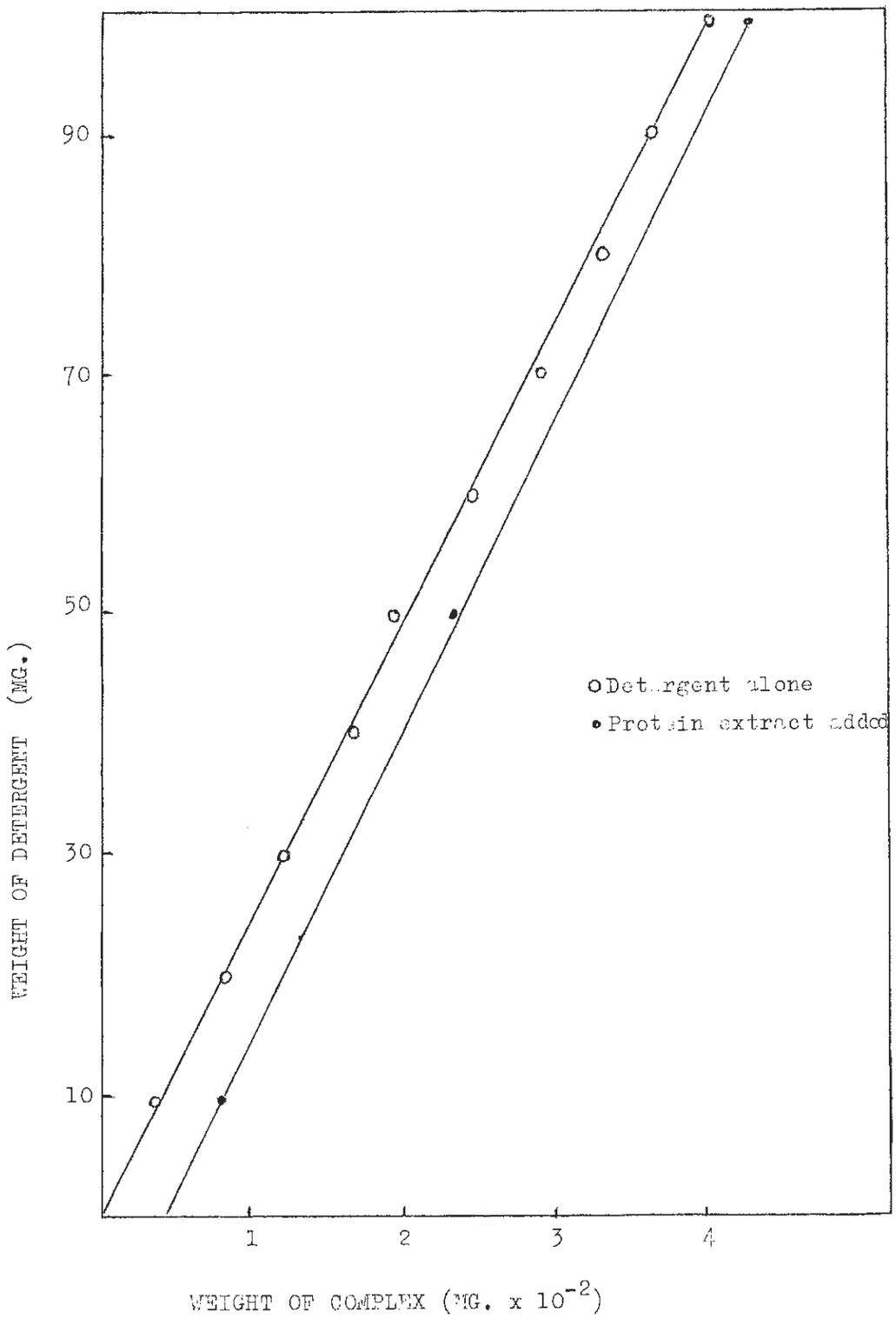


Fig. 22. Calibration curve for Tergitol NPX, showing the effect of added protein degradation material.

TABLE 21

Equations of the phosphotungstic acid calibration curves for various detergents where y = weight of detergent (mg.) and x = weight of complex (mg.)

Detergent	Regression Equation	S.E. of b	Residual S.D.	Correlation coefficient
Tergitol NPX	y = 0.2454x - 0.0948	0.0108	2.1838	0.9977
Lissapol NX	y = 0.2459x + 1.8684	0.0134	1.7565	0.9985
Fluidol W100	y = 0.2505x + 0.0077	0.0076	1.0490	0.9995
Triton N100	y = 0.2366x + 0.7855	0.0062	0.8116	0.9997
Tergitol 12P9	y = 0.2566x + 8.8212	0.0616	14.6007	0.7966

It will be seen that the slopes are all of the same order and that, in all cases but the last one (Tergitol 12P9) the straight line postulate was an extremely good one. Once again, very little spread of points occurred around the predicted lines.

The case of Tergitol 12P9 was investigated in more detail and after a considerable number of duplicate determinations it was found that no improvement could be made to the spread of points around the regression line. The experimental points and the regression line for this detergent are shown in Fig. 21. The results of the determination with Tergitol NPX in the presence of degraded protein material are shown in Fig. 22.

Discussion:

It will be seen from Fig. 20 and Table 21 that this method gives an accurate and precise calibration curve when applied to pure aqueous solutions of nonionic detergents. Very high correlation coefficients were obtained in all cases with the exception of Tergitol 12P9. The method has one great advantage over the phosphomolybdic acid procedure, viz. that the precipitate

can be weighed within 2 hours of precipitation. The accuracy of this method is of the same order as that obtained with the phosphomolybdic acid procedure.

The case of Tergitol 12P9 raises an interesting point which seems to have been neglected by previous investigators. This detergent is a derivative of dodecylphenol containing 9 moles of ethylene oxide, which makes the molecule somewhat hydrophobic. It has, in fact, a cloud point of only 18°C (in 0.5% aqueous solution). According to Maclay[51] and other workers[108,109], a solution of a nonionic detergent, when stored at temperatures above its cloud point, separates into two phases, one which is rich in detergent and another which is water-rich. It is obvious that the distribution of the detergent in such a system would be extremely heterogeneous. The temperature at which the determinations were carried out was rarely less than 20°C, i.e. 2°C above the cloud point of the detergent. The two phases were clearly discernible when the solution (0.5% aq.) had been standing for some time. Aliquots were drawn from this solution after thorough shaking by hand, and it is felt that the erratic results obtained may be ascribed to the fact that the detergent was still unevenly distributed in the sample. This is a difficulty which would arise with all detergents which have a very low cloud point (below room temperature). This complication is a further limitation of the method and it will affect the determination with phosphomolybdic acid in a similar way. The results obtained with Tergitol 12P9 are far too erratic for use as a calibration standard.

It will be seen from Fig. 22 that the addition of the protein fraction causes an appreciable increase in the weight of the precipitate obtained. This is due to the fact that the protein

material is precipitated by the phosphotungstic acid under the conditions of the determination as suggested by Fong[3]. Fig. 22 therefore offers proof that the method is indeed sensitive to the presence of protein degradation material.

8.2.3 Spectrophotometric method.

Introduction:

Of the spectrophotometric methods, that of Brown and Hayes[93] was best suited to the needs of this study. This method has, in fact, been used by Fong[3] to estimate the amount of nonionic detergent remaining in scouring effluents. He found a direct ultraviolet spectrophotometric method unsuitable since the effluents contained UV-absorbing substances, e.g. water-soluble suint and soluble protein degradation products. It has recently been shown by Anderson[110] that there is also a small contribution by wool grease at 275 mμ. Unfortunately it was not possible to carry out the preliminary clarification of the solution in this laboratory since it involves the use of an ultra-centrifuge[3] and therefore it was decided to use the direct UV-spectrophotometric method reported by Griffith[92] on solutions which would be kept as free of interfering substances as possible.

Reagents and equipment used:

Detergent solutions were made up in distilled water using a sample of 100% active Tergitol NPX supplied by the manufacturer.

The spectrograms were recorded on a Unicam SP700 recording spectrophotometer.

Experimental:

It has been reported by Griffith[92] that the peak at 278 mμ can be used for the estimation of nonionic detergents. In this

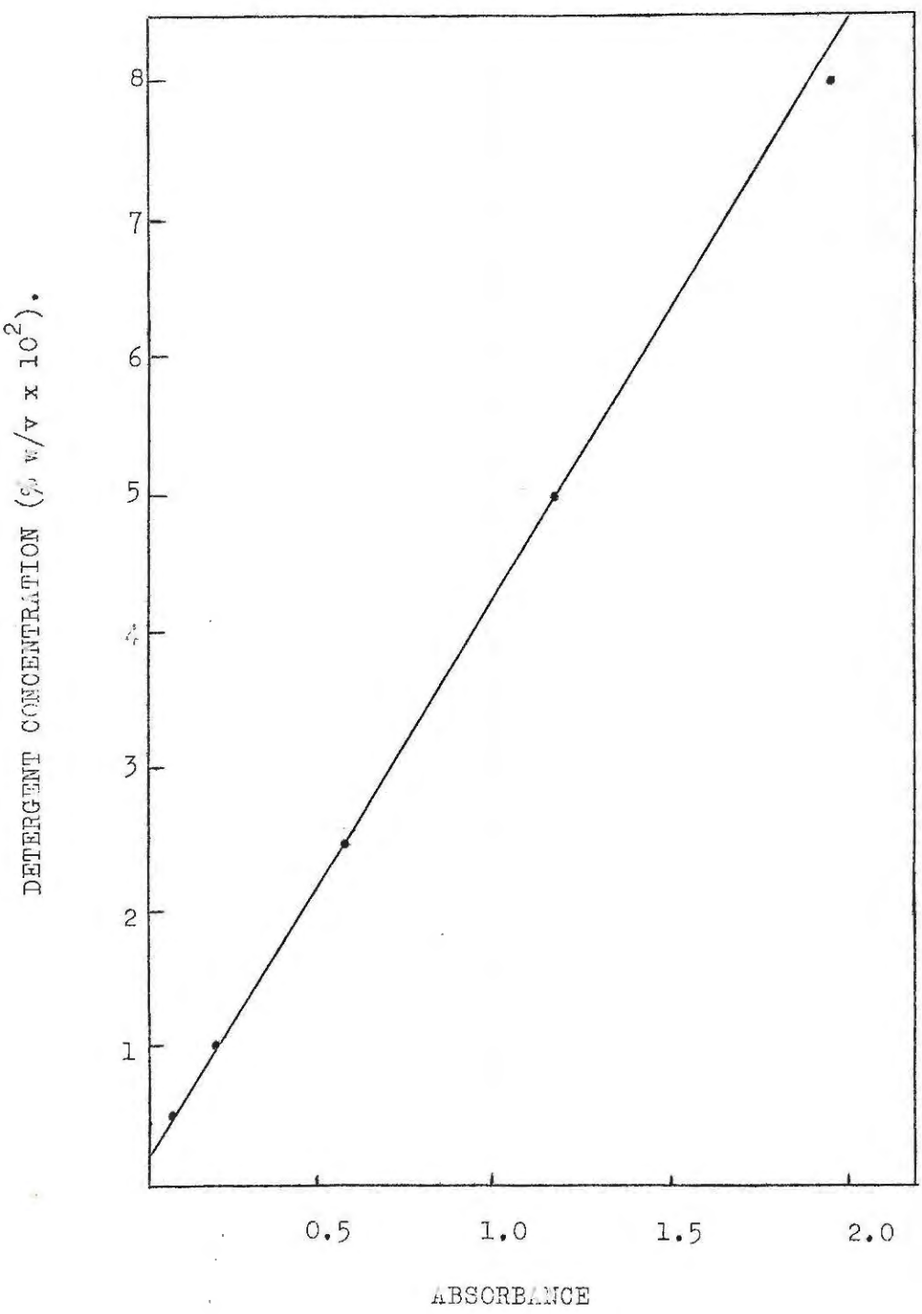


Fig. 23. Calibration curve for Tergitol NPX using a 10 mm. silica cell.

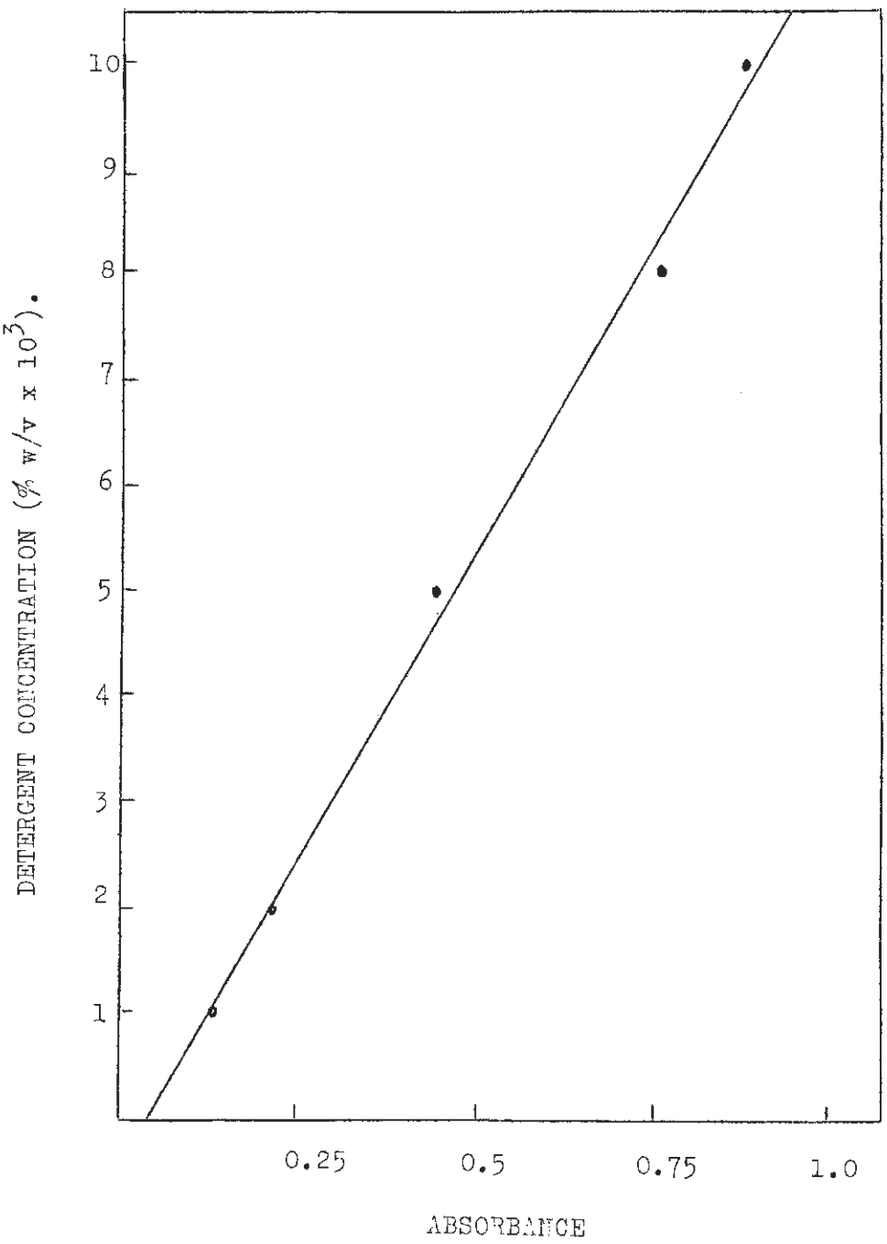


Fig. 2. Calibration curve for Tergitol NPX using a 40 mm. infrasil cell.

study, nonionic detergents were found to give two peaks, one at 224 mμ and another at 276.3 mμ; the latter having a small shoulder at about 282 mμ. A trace similar to the ones obtained here has been published by Walz and Kirschnek[111]. As a result of a scratched collimating mirror in the instrument, an excessive amount of stray light was present in the lower wavelength regions. The peak at 224 mμ could therefore not be tested for quantitative use, and it was decided to use the peak at 276 mμ for determining the calibration standards. Some stray light was still evident and its presence was corrected for as follows: instead of setting the zero transmission line by blanking out the sample beam, it was set by filling the sample cell with a solution of detergent which was just sufficiently concentrated to give zero transmission at the wavelengths used. A concentration of 0.25% w/v of Tergitol NPX was found suitable. The calibration curve obtained in this way using a 10 mm. silica cell is shown in Fig. 23. It will be seen that the straight line drawn through the points is an excellent fit.

To investigate the behaviour of very dilute detergent solutions, a second calibration curve was drawn for concentrations from 0.001% to 0.01%. The zero transmission line was set as above and a 40 mm. infrasil cell was used at 276 mμ. The calibration curve obtained is shown in Fig. 24.

The molecular extinction coefficient calculated from the results $E^{1\%}_{1\ cm}(276.3)$, is 24.7. This value, when compared with those of Walz and Kirschnek[111], would give Tergitol NPX an ethylene oxide molecular ratio of slightly higher than 10, which is in good agreement with the figure supplied by the manufacturer. viz. 10.5.

Discussion:

It will be seen that the direct spectrophotometric method can be applied to solutions of Tergitol NPX in distilled water. The accuracy falls off somewhat in the lowest concentration ranges (down to 0.001% w/v), which should therefore be avoided.

It follows from the method that all substances which absorb at the wavelengths used should be absent. It has been reported that the water soluble suint, protein material[3] and wool grease[110] absorb in these regions.

It seems that there is scant hope of applying this direct method to concentration control in scouring and that its use should be restricted to pure aqueous solutions. Extremely low detergent concentrations should be avoided.

8.2.4 Polarographic method.

Introduction:

Some thought was given to the possibility of using polarographic methods for the estimation of the excess phosphotungstic acid from the determination of Barber et al[82]. As far as could be ascertained, no polarography has as yet been carried out on phosphotungstic acid, but the behaviour of tungstate ions at a dropping mercury electrode has been reported by several investigators. Lingane and Small[112] and von Stackelberg et al[113] have shown that tungstate ions are reduced at a mercury electrode in a concentrated hydrochloric acid solution (8 - 12 M). It was thought that this characteristic could be adapted to the determination of phosphotungstic acid.

Reagents and equipment used:

The polarograms were recorded on a Metrohm Polarecord

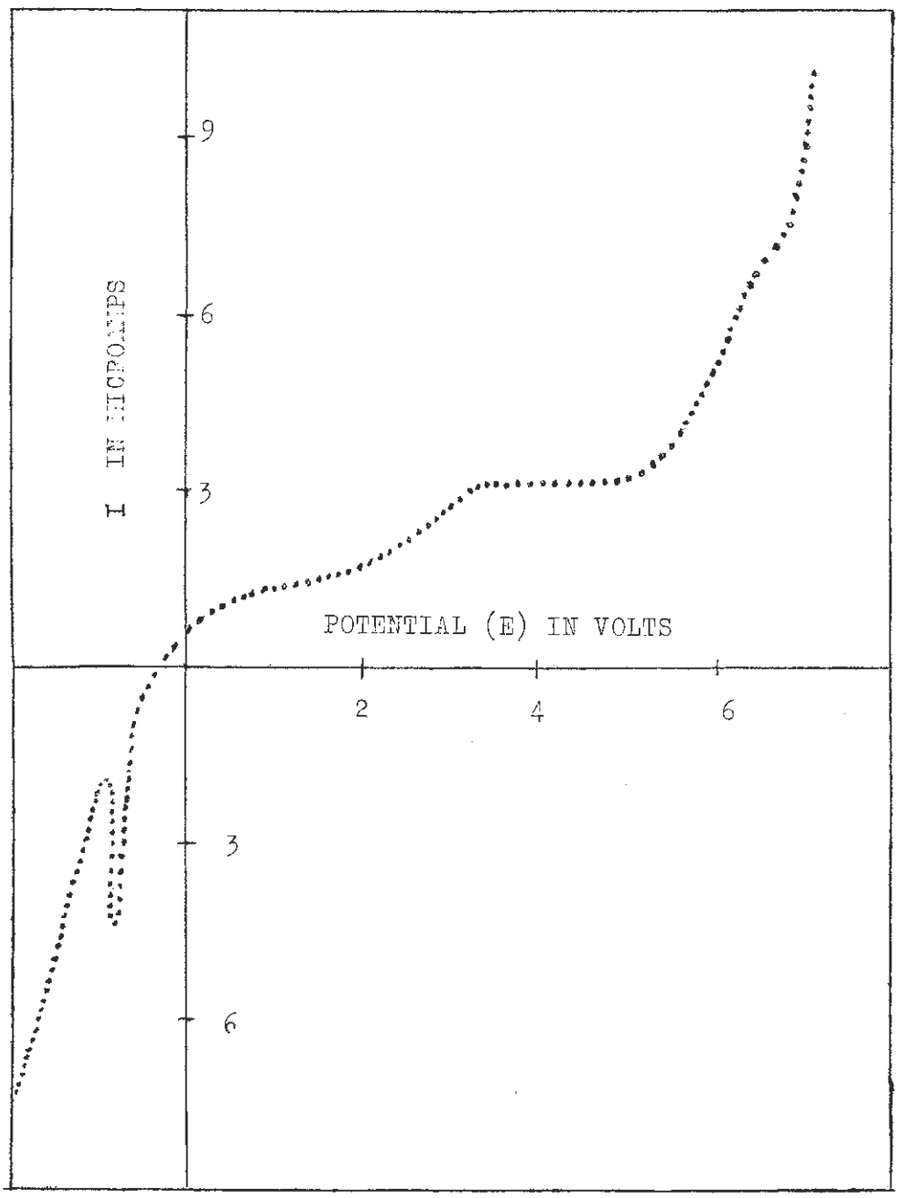


Fig. 25. Polarogram of 10^{-3} M phosphotungstic acid in 2.2N HCl supporting electrolyte.

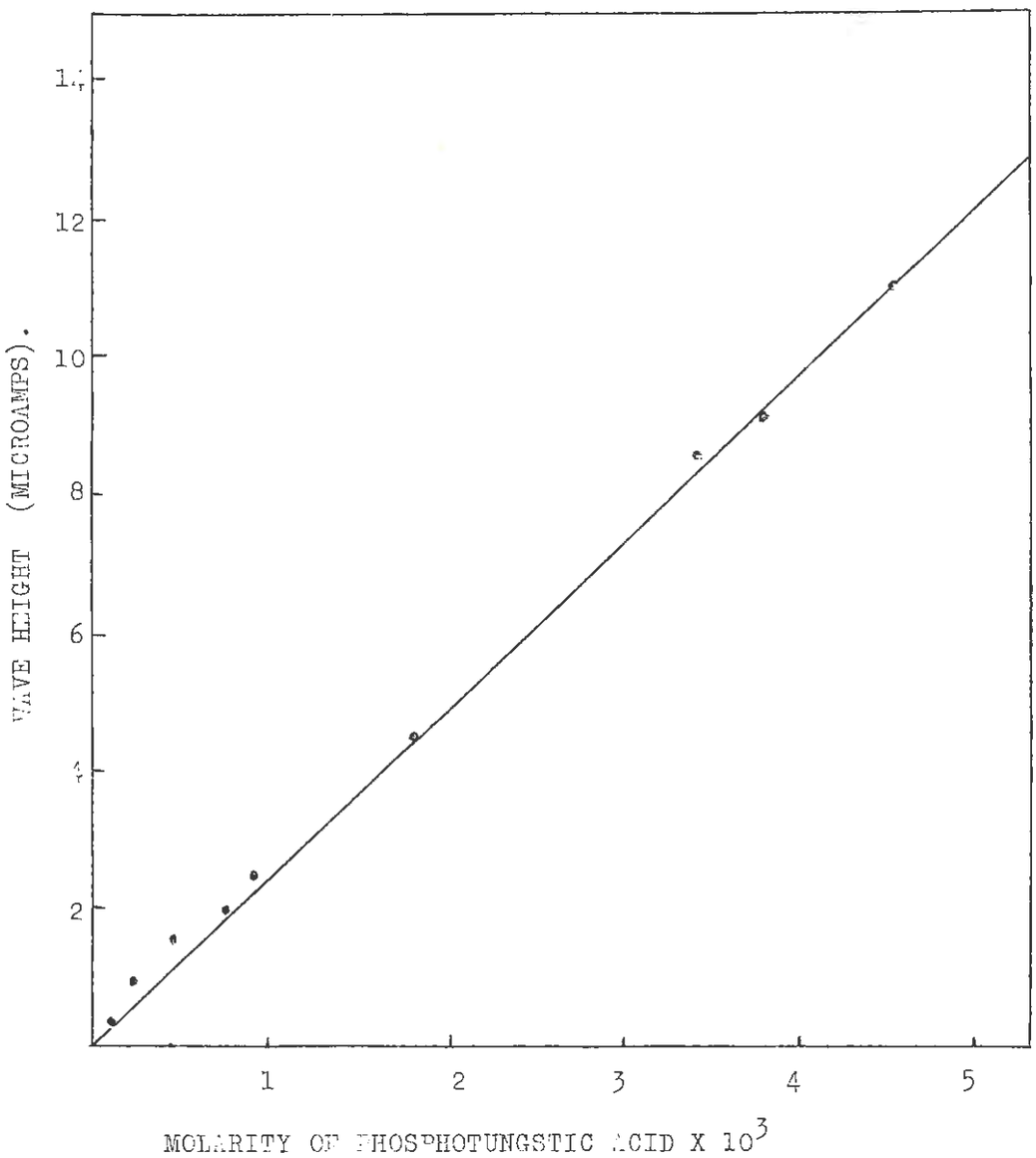


Fig. 26. Variation of wave height of phosphotungstic acid waves with concentration.

Type E261R recording polarograph. The capillary had m and t values of 3.12 mg/sec. and 3 sec. respectively which gave a capillary constant ($m^{2/3}t^{-\frac{1}{2}}$) of 2.68 $mg^{2/3}$ $sec^{-\frac{1}{2}}$. All voltages given are with reference to an Ag/AgCl electrode (S.S.E.)

All solutions were made up in distilled water, using analytical grade reagents whenever possible.

Experimental and Results:

On investigation of the published work[112,113], it was found that phosphotungstic acid was precipitated by HCl solutions of the high concentrations used (8 - 12M). Suitable polarograms could, however, be obtained with phosphotungstic acid solutions in 2.2M HCl medium as shown in Fig. 25. The wave with the half-wave potential at approximately -0.25 volt was used for the analyses. The wave-heights were determined at several concentrations of phosphotungstic acid and the results plotted in Fig. 26. The curve is a straight line which extrapolates to zero at zero concentration.

An attempt was then made to determine the concentration of phosphotungstic acid in the mother liquor of the precipitation mixture of Barber[82] (see 8.2.2) using the above calibration curve. The normal procedure was found to give a supernatant liquor which contained phosphotungstic acid in very low concentrations at which point the method was not as accurate as in the intermediate ranges. At this stage, two possible solutions were considered, viz.

a) to concentrate the mother liquor by modifying the precipitation reaction in order to be able to work in the most linear region of the calibration graph, or

b) to find a more sensitive method for the determination, e.g. the utilization of a catalytic hydrogen wave of the type used by Brdicka[114] for the determination of thiol groups.

In an investigation of the first alternative, the 200 ml. distilled water was omitted, the procedure being as follows: 10 ml. each of 10% phosphotungstic acid and 10% $BaCl_2$ solution was added to a specific volume of nonionic detergent of known concentration. Then 2.5 ml. of concentrated HCl was added and the mixture boiled for the required time. After cooling the solutions were made up to 50 ml. (sufficient concentrated HCl was added to bring the solutions to the required 2.2M HCl concentration). The precipitate was centrifuged off and a polarogram was run on the supernatant liquor. The results which are shown in Table 22 seemed to favour a straight line but were too erratic to be of any analytical value. Subsequent repetitions of this investigation caused no improvement in the scatter of the points.

TABLE 22

Concentrations of phosphotungstic acid in mother liquor of precipitation solution

mg. Tergitol NPX precipitated	wave height obtained in microamps	Concentration of phosphotungstic acid in supernatant liquor
20	12.3	5.00×10^{-3}M
30	10.9	4.46×10^{-3}
50	10.7	4.38×10^{-3}
70	9.9	4.06×10^{-3}
80	9.6	3.94×10^{-3}
90	7.8	3.20×10^{-3}
100	8.9	3.64×10^{-3}

This procedure was abandoned in view of the unreliable results obtained.

The second alternative, (b) above, was then investigated. After a preliminary investigation at room temperature it seemed

that this method held some promise and a calibration curve was established as follows:

A base solution, called solution N, was made up as follows: 85 g. NH_4Cl, 56 ml. 25% ammonium hydroxide, 37 g. KCl, 50.4 g. $Na_2SO_3.7\ H_2O$, 10 ml. 0.1M $CoCl_2$ and 5 ml. 2.5% gelatin were made up to one litre. The pH of this solution was 9.3. 10 ml. of solution N was pipetted into a water-jacketed polarography cell, the temperature of which was kept constant at 31°C, 1 ml. of 10^{-3}M phosphotungstic acid was added and hydrogen passed through the solution for 10 minutes. Since sulphite effectively removes dissolved oxygen from solutions at high pH, the purpose of the hydrogen passed through the solution was only to obtain a homogeneous mixture and to accelerate equilibration of temperature and not to remove interfering gases. The initial addition of phosphotungstic acid was necessary since more reproducible results could be obtained when the change in an existing wave was measured than when original waves were compared. This was probably due to small amounts of impurities which reacted with the phosphotungstic acid and were removed by the presence of a slight excess of phosphotungstic acid before measurements were started.

Polarograms were recorded between -1.35V and -1.75V. The polarogram obtained from the above procedure was called the base polarogram. Subsequent polarograms were recorded after additions of specific quantities of phosphotungstic acid solution to the base solution. The solutions were mixed after each addition by passing hydrogen gas through the cell for one minute. The height of the wave in the base polarogram was subtracted from the height of the catalytic wave obtained for each addition of phosphotungstic acid. This difference, H (in microamps) was plotted

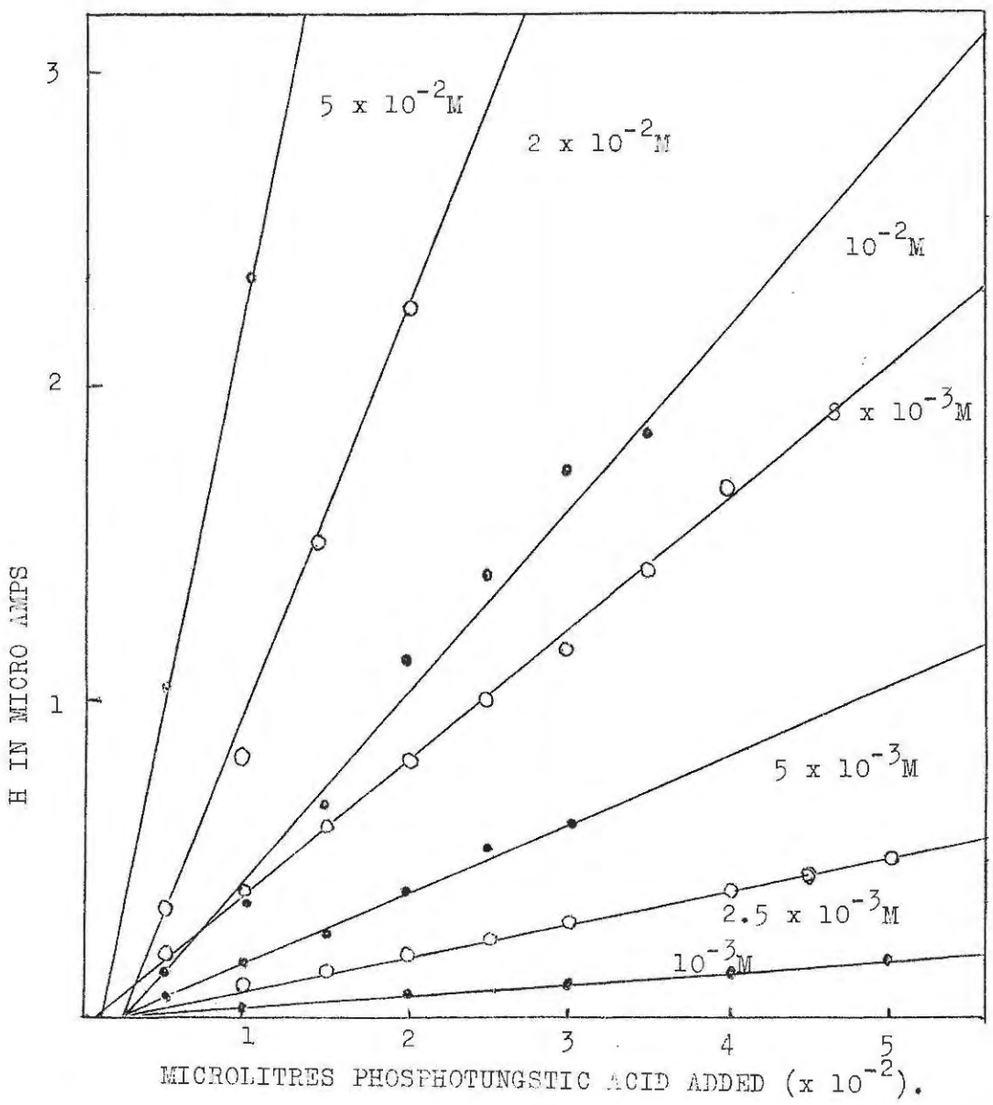


Fig. 27. Heights of catalytic hydrogen waves above base polarogram for various additions of phosphotungstic acid.

against the quantity of phosphotungstic acid added as in Fig. 27. The slopes of these lines were calculated and compared with the concentration of the phosphotungstic acid solutions used in determining them. The results obtained are given in Table 23.

TABLE 23

Slopes (in μA/μlitre x 10^3) of lines obtained with various concentrations of phosphotungstic acid. (From Fig. 27).

Concentration (Molar)	Slope
2.5×10^{-4}	0.036
5×10^{-4}	0.136
10^{-3}	0.400
2.5×10^{-3}	1.05
5×10^{-3}	2.2
8×10^{-3}	4.2
10^{-2}	5.8
2×10^{-2}	12.8
5×10^{-2}	26.0

An attempt was then made to use the calibration curve drawn from Table 23 for the estimation of the concentration of phosphotungstic acid in the mother liquor of the precipitation mixture. It was found that the presence of Ba^{++} caused the gelatin to precipitate with the phosphotungstic acid. The Ba^{++} had to be removed by precipitation with 1 g. Na_2SO_4 and the precipitate was centrifuged off. The results obtained were even more erratic than those from the first method.

Discussion:

A reasonably accurate method for the estimation of phosphotungstic acid was obtained from the polarograms of phosphotungstic acid in hydrochloric acid supporting electrolyte.

The mother liquor from the Barber[82] determination of nonionics contained phosphotungstic acid in very low concentrations. The results obtained from a more concentrated mother liquor were too erratic to be of any value as an analytical method. The second method investigated, in which a catalytic hydrogen wave was produced, gave good calibration curves for pure phosphotungstic acid solutions. Erratic results were obtained when the method was applied to the mother liquor obtained when a nonionic detergent had been precipitated with phosphotungstic acid. The erratic results were probably due to adsorption of the phosphotungstic acid on the nonionic-phosphotungstic acid precipitate and on the $BaSO_4$ precipitate formed when the barium ions were removed from the solutions. It was concluded that the amount of phosphotungstic acid present in the mother liquor was not a reliable indication of the amount of nonionic detergent precipitated.

9. SORPTION OF NONIONIC DETERGENTS.

9.1 INTRODUCTION

The distinguishing characteristic of surface-active compounds is that they are unbalanced, a molecule of such a compound consisting of two parts; a water-compatible or hydrophilic part and an oil-compatible or hydrophobic part[115,116]. This characteristic causes inherent instability in aqueous solutions, which is partly overcome by two main effects, viz. the formation of micelles[117] and orientation at interfaces[118]. The second factor is partly responsible for the ability of these compounds to cause wetting, emulsification and detergency. The air surface and the surface of the vessel containing a detergent solution are normally more compatible with the hydrophobic part of the molecule than water. When a detergent molecule is aligned with the hydrophobic part adjacent to the air or other surface and the hydrophilic part in the water[119], the inherent instability is partly overcome. Surface-active molecules will therefore tend to concentrate at the interface and this phenomenon is known as adsorption.

A clean wool fibre is not readily wetted by water since its surface may be supposed to consist principally of hydrocarbon chains with perhaps a few $-NH_2$, -COOH and -CONH- groups[120]. A fairly closely packed film of detergent molecules adsorbed at this interface is therefore oriented with the hydrophilic heads towards the water.

A considerable amount of work has been done on the sorption of ionic, viz. both anionic and cationic detergents on wool and cotton. The sorption of soap by wool has been measured

by various workers[49,121] and it was shown that sorption took place in the form of molecules rather than micelles[122]. Synthetic detergents such as sodium alkyl sulphates and alkyl aryl sulphonates are also sorbed by wool[49,121,123]. The sorption of the ionic detergents passes through a maximum and sometimes subsequently a minimum as the concentration of surface-active material in the aqueous phase is increased. Until 1949 only Aickin[124] had reported these fluctuations, but this observation has since been verified by several investigators[49]. In a study of the rate of sorption of sodium cetyl sulphate by wool at 50°C, Swanston and Palmer[123] explained their results as follows: the ions in solution are Na^+ and Det^-, the latter of which has an affinity for the wool and diffuses into the fibre from the solution. At the same time the Na^+ diffuses into the wool to preserve stoichiometric neutrality. It should be borne in mind that Na^+ would not normally be expected to have any affinity for the wool[125] and it must be assumed that they are simply drawn in by the electrical attraction of the detergent ions. Then, as the concentration of NaDet in the wool builds up, the nett rate of sorption of NaDet decreases because of the growing importance of the back diffusion of Na^+ and Det^- ions.

It was found by Harris[126] that the amounts of anionic and cationic detergents sorbed by wool were considerably more than those sorbed by cotton. The amount of sorption on wool depended on the pH conditions, time of sorption, temperature, the nature of the surface-active agent, and concentration conditions. These observations were confirmed by Meader and Fries[49] who concluded that the adsorption on cotton was purely physical, whereas the sorption on wool was a combination of physical and chemisorption.

Further, the adsorption of fatty acid soaps[127], sodium oleate[128], sodium dodecyl sulphate[129] and alkylaryl sulphonates[130] has also been measured. The effect of detergent builders on the sorption of detergent by cotton was investigated by Boyd and Bernstein[131] who found that cotton adsorbed less detergent in the presence of $Na_4P_2O_7$ than when Na_2SO_4 was used as a builder. The presence of NaCl caused no change in adsorption of detergent.

It will be seen from the above that much work has been done on the sorption of ionic detergents on various textile fibres, but an exhaustive literature survey revealed that very little fundamental work had been done on nonionic detergents. It appears that there are several reasons for this, the most important of which is probably the distribution of the ethylene oxide mole ratio generally found in nonionic detergents. Even when the detergent is prepared from molecularly homogeneous intermediates the resulting condensate is a mixture of compounds with different molecular weights, although it has recently been reported[132] that a pure nonionic detergent has been synthesised. Mayhew and Hyatt[62] found that the weight percentage distribution of the reaction products of nonyl phenol with ethylene oxide fits a Poisson distribution as had been predicted by Flory[133] from theoretical considerations. The ethylene oxide content of the final product is normally expressed as an average figure which is fairly accurate. Another, perhaps less basic reason is that there are no really accurate and rapid methods available for the estimation of nonionic detergents[134,135]. Also, because the nonionic detergents do not ionise when dissolved in water, the tendency to adsorption by wool is less and smaller amounts of sorption have to be measured. It is obvious that reliable and accurate

methods are required to measure these small differences in concentration.

It is perhaps because of the small tendency to adsorption of the nonionic detergents that most of the work on nonionic detergent adsorption has been carried out on substrates which are known to be strong adsorbers. Thus, the adsorption of polyoxyethylated nonyl-and octylphenols on quartz powder (0.5 to 4μ) has been reported[136]. The extent of maximum adsorption was not changed appreciably by changing from nonyl- to octylphenol. The maximum adsorption was expressed as

$$\max = \frac{250}{R^{1.45}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.1)$$

where R = mole ratio of ethylene oxide to phenol

From this, it seems that the length of the ethylene oxide chain plays a more important role in determining the maximum adsorption than does the hydrophobic part of the molecule. This was confirmed by Abe and Kuno[137] in their study of the adsorption on hydrophobic carbon black in which they found that the adsorption decreased with increasing ethylene oxide chain length. They considered this to be due to the fact that the adsorptional cross-sectional areas are increased as the ethylene oxide chain length increases and that the only effect operating is that of molecular size. Abe and Kuno also investigated the sorption onto hydrophilic $CaCO_3$[138] where they found marked changes in the adsorption isotherms with differing ethylene oxide chain lengths. Bell[139] found an increase in the adsorption of an ethylene oxide condensate with propylene on 45 to 60 mesh sand with increasing concentration of detergent. With an alkyl-aryl polyether alcohol, however, the sorption reached a maximum at which it

remained constant, and it was observed that the surface tension depressions showed the same trends in both cases. An attempt was made at explaining the results in terms of the following equilibrium:

micelles in soln. $\rightleftharpoons$ single mols. in soln. $\rightleftharpoons$ mols. adsorbed at surface.

In the former case there is little micelle formation to compete with the adsorption process and the degree of adsorption continues to increase.

The adsorption of nonionic detergents by wool was measured by Le Compte and Creely[55]. Of the two nonionics investigated, one gave very low adsorption compared to the ionic detergents tested and the other consistently indicated negative adsorption in alkaline, acid and neutral solutions. Admittedly, the gravimetric method used for determination of the nonionic detergent is open to some criticism, but they claim to have verified their results by a drop number method.

In an attempt to relate adsorption with detergency McLaren[34] found some difficulty in detecting the amount of detergent sorbed. At high temperatures in the region of 80° to 90°C, no adsorption could be detected. It is likely that some adsorption did take place since the wool was wetted by the solution but the amount sorbed was less than 0.05 g. per 100 g. dry wool. The addition of acid caused an increase of sorption by the substrate which actually causes a decrease in detergency by reducing the concentration of free detergent below that necessary to keep the soil which has already been detached in suspension. The mechanism was thought to be firstly the conversion of the soap on the commercial serge to its free fatty acid and subsequently the combination of detergent and fatty acid by means of hydrogen bond formation

between the hydroxyl group of the acid and ether oxygen atomsin the detergent. In the presence of sodium chloride, no adsorption by the fibres could be detected until the critical concentration of salt at which the detergent started precipitating was reached. Here, the precipitated detergent was being removed from the solution by filtration by the wool rather than by adsorption.

Weatherburn and Bayley[54] compared the sorption of all types of detergents, (anionic, cationic and nonionic) on various types of textile fibres. The sorption, x(in millimoles of compound per gram of dry fibre) was calculated as follows:

$$x = \frac{2.5\ (C_o - C)}{(100 - A)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.2)$$

where C_o = concentration of solution before contact with fibres (in m.moles/litre)

C = concentration of solution after contact with fibre (in m. moles/litre)

A = moisture content of conditioned fibre (%)

The general level of sorption of the nonionics was remarkably low compared to the sorption of anionics especially in the case of wool, which did not sorb the nonionics to any appreciable extent. The degree of sorption decreased slightly with increasing length of the ethylene oxide chain over the range investigated. The variation of sorption with concentration showed a break at the critical micelle concentration. It was concluded that single long-chain ions are sorbed at concentrations above and below the critical micelle concentration, probably in accordance with the Freundlich adsorption isotherm

$$x = kC^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9.3)$$

where x = quantity sorbed

C = equilibrium concentration

n and k = constants.

It was confirmed that the sorption of nonionic detergents is more marked under acid than alkaline conditions.

The aim of this study was to determine the magnitude and rate of adsorption of nonionic detergents onto wool and various other impurities present in scouring liquors under controlled conditions. The methods used for the estimation of the concentrations were those investigated in the previous chapter. A new indirect method, which gives an indication of the amount of detergent sorbed by impurities in scouring liquors, was also investigated.

9.2 EXPERIMENTAL

9.2.1 Using phosphomolybdic acid for the determination of nonionic detergent.

Method:

One gram samples of wool cloth (average fibre diameter approximately 21μ) which had been extracted with ether and alcohol in a soxhlet for two days and conditioned for 48 hours at $20^{\circ} \pm 1^{\circ}C$ and $65 \pm 2\%$ R.H. were used. The samples were left in contact with 20 ml. solution contained in stoppered test tubes which were immersed in a water-bath at $25^{\circ}C$. The solutions contained 20 mg. Berol Lanco. The samples were not agitated during the time of adsorption, but immediately after the stated periods had elapsed, the tubes were shaken to distribute the detergent evenly throughout the solution before the aliquots (10 ml.) were withdrawn. The amount of detergent present was determined using the phosphomolybdic acid method. (See 8.2.1).

The above procedure was repeated using 0.5 g. of conditioned loose wool which had been cleaned by washing in ether, alcohol and hot water. Contact with detergent was avoided at all stages in the

cleaning process. The burrs and other vegetable matter were removed by teasing on hand-cards. The samples were left in contact with 10 ml. of solution containing 10 mg. Lissapol NX. Aliquots of 5 ml. were withdrawn as above and the detergent content determined.

The same procedure was also used in an attempt to establish the effect of the diameter of the wools used on the degree of sorption. Samples of 0.5 g. of cleaned, conditioned wool of different diameters (16,18,20,22,24 and 26μ) were left in contact with 20 ml. of solution containing 100 mg. Tergitol NPX at 25°C. The aliquots (10 ml.) were taken and analysed as described above.

Results:

Some of the results obtained in the experiments are given in the Tables below.

TABLE 24

Sorption of Berol Lanco by wool cloth at 25°C
(Wool:liquor ratio 1:20)

Sorption time (hr.)	Original concn. (mg./10 ml)	Concn. after sorption (mg./10 ml)	Detergent sorbed (mg.)
1	10	9.0	1.0
2	10	10.1	-0.1
2.5	10	8.7	1.3
3.5	10	9.3	0.7
4.5	10	8.6	1.4
5	10	8.7	1.3

TABLE 25

Sorption of Lissapol NX by cleaned loose wool at 25°C
(Wool:liquor ratio 1:20)

Sorption time (hr.)	Original concn. (mg./10 ml)	Concn. after sorption (mg./10 ml)	Detergent sorbed (mg.)
1	10	10	0.0
2	10	10.2	-0.2
3	10	11.0	-1.0
4	10	9.8	0.2
5	10	10.0	0.0

TABLE 26

Sorption of Tergitol NPX by cleaned loose wool of different diameters at 25°C (wool:liquor ratio 1:40)

Ave. Diam. (μ)	Sorption time (min.)	Original concn. (mg./10 ml)	Concn. after sorption (mg./10 ml)	Detergent sorbed (mg.)
16	5	50	49.0	1.0
16	10	50	48.8	1.2
16	15	50	50.8	-0.8
16	30	50	50.0	0.0
16	60	50	50.5	-0.5
18	5	50	50.0	0.0
18	10	50	50.8	-0.8
18	15	50	50.8	-0.8
18	30	50	50.5	-0.5
18	60	50	51.1	-1.1
20	5	50	50.3	-0.3
20	10	50	50.7	-0.7
20	15	50	50.7	-0.7
20	30	50	48.7	1.3
20	60	50	50.5	-0.5
22	5	50	50.7	-0.7
22	10	50	50.8	-0.8
22	15	50	51.0	-1.0
22	30	50	50.9	-0.9
22	60	50	51.3	-1.3
24	5	50	50.5	-0.5
24	10	50	50.3	-0.3
24	15	50	50.5	-0.5
24	30	50	50.3	-0.3
24	60	50	50.3	-0.3
26	5	50	50.5	-0.5
26	10	50	50.7	-0.7
26	15	50	50.7	-0.7
26	30	50	50.5	-0.5
26	60	50	52.0	-2.0

Discussion:

It will be seen from all the results that there is only a very small change in concentration and it is doubtful whether the estimation procedure is capable of distinguishing between such small changes.

The concentration changes found were virtually consistently changes to higher concentrations, indicating negative sorption. These results agree with the published work of Le Compte and Creely[55]. McLaren[34] in several instances reported that he was unable to detect any sorption; however, the wool was wetted which indicates that some sorption, however small, must have taken place.

Preferential sorption of water by the wool may have been responsible for the seemingly anomalous results, but this was thought unlikely since some investigators[34,54] found it unnecessary to apply a correction for the water sorbed by the wool to attain its saturation moisture content (35 to 36%). Nevertheless it was deemed necessary to investigate this aspect in order to obtain the most accurate results possible. Another aspect which had to be investigated further was the concentration of the sorption solutions. In view of the very small concentration changes involved it was thought that a decrease in the concentration of the original sorption solution would make any changes which did occur relatively more marked and easier to measure. It was decided to use the spectrophotometric method for the determinations because of the low concentrations to be used.

Another factor which may have caused the higher concentrations after sorption is the possibility that a local excess may have formed in the vicinity of the wool. It was hoped that the method used for collection of the aliquot would have minimised this effect, but it was nevertheless decided to experiment with different methods of collecting the aliquots in order to ensure that such local excesses, if present, would not interfere with the results.

9.2.2 Using the spectrophotometric method for the determination of nonionic detergent.

9.2.2.1 Sorption by wool from relatively concentrated solutions.

Method:

All the sorption measurements were carried out using Tergitol NPX as detergent. The calibration curves are given in Section 8.2.3.

In view of the fact that preferential water sorption or some similar effect was indicated by the phosphomolybdic acid determinations, it was decided to conduct the preliminary investigations with the spectrophotometric method under the same conditions in order to establish whether the same trends would be exhibited in this case.

The same sorption procedure was used as before, i.e. the wool was placed in contact with the solutions which were contained in stoppered test tubes immersed in a thermostat at 25°C. After the time of sorption had elapsed, the aliquot was withdrawn and analysed as described in 8.2.3.

In the first series 0.5 g. conditioned wool was used together with 20 ml. approximately 0.5% w/v Tergitol NPX solution. Two types of wool with different average diameters (16, 18μ) were used, and two methods were used for collecting the aliquot. In the first, the supernatant liquor was poured off immediately after the sorption period had elapsed (the "pour" method). In the second, the supernatant liquor was also poured off, but then the test tube was inverted and the wool squeezed with a glass rod to expel as much as possible of the liquor trapped by the wad of wool (the "squeeze" method). In both cases a 10 ml. aliquot was

pipetted out and diluted to 200 ml. for estimation in the spectrophotometer. The absorbance of the sample was measured at 276 mμ in a 10 mm. silica cell. These experiments were repeated at 35°C, using the 16μ wool.

In the next series an attempt was made to evaluate the effect of preferential sorption of water by wool which is not completely saturated with water. For this purpose a series of wool samples was saturated with water before they were placed in the sorption solutions. The samples were prepared as follows: two series of 0.5 g. samples of conditioned wool (16μ and 18μ) were weighed out and soaked in water for 1 hour at the temperatures at which the sorption measurements were to be carried out (25°C). After an hour had elapsed, the samples were squeezed out between two watch-glasses and reweighed. These reweighed samples (see Table 29) were then used for the sorption determinations. The aliquots (10 ml.) were collected by the "pour" method, diluted to 200 ml. and analysed as above. In the second series (18μ) the aliquots were diluted to 250 ml.

Results:

The results obtained in the above investigations are shown in the Tables following.

TABLE 27

Sorption of Tergitol NPX by wool at 25°C(Wool:liquor ratio 1:40)

Ave. Diam. of wool(μ)	Sorption time (min.)	Method for collecting aliquot	Blank concn. (% w/v)	Concn. after sorption (% w/v)
16	5	Pour	0.025	0.0273
16	15	Pour	0.025	0.028
16	30	Pour	0.025	0.0275
16	5	Squeeze	0.025	0.0283
16	15	Squeeze	0.025	0.0284
16	30	Squeeze	0.025	0.0283
18	5	Squeeze	0.029	0.027
18	15	Squeeze	0.029	0.0277
18	30	Squeeze	0.029	0.0277
18	5	Pour	0.029	0.0273
18	15	Pour	0.029	0.027
18	30	Pour	0.029	0.0283

TABLE 28

Sorption of Tergitol NPX by wool of 16μ diameter at 35°C

(Wool:liquor ratio 1:40)

Sorption time (min.)	Method for collecting aliquot	Blank concn. (% w/v)	Concn. after sorption (% w/v)
5	Pour	0.026	0.0277
15	Pour	0.026	0.028
30	Pour	0.026	0.0283
60	Pour	0.026	0.0285
5	Squeeze	0.026	0.0277
15	Squeeze	0.026	0.0283
30	Squeeze	0.026	0.0283
60	Squeeze	0.026	0.0283

TABLE 29

Sorption of Tergitol NPX by water-saturated wool samples at 25°C

(Wool:liquor ratio 1:40)

No correction was applied for dilution effect

Ave. Diam. (μ)	Sorption time (min.)	Blank concn. (% w/v)	Concn. after sorption (% w/v)	Weight of saturated samples (g.)
16	5	0.0254	0.0250	1.6112
16	10	0.0254	0.0254	1.2358
16	15	0.0254	0.0254	1.5180
16	30	0.0254	0.0254	1.4348
16	60	0.0254	0.0250	1.4769
18	30	0.021	0.021	1.3940
18	30	0.021	0.021	1.3572
18	30	0.021	0.0214	1.3740
18	30	0.021	0.0213	1.3760

Discussion:

From Tables 27 and 28 it may be seen that there is no significant difference in the results obtained using the two different methods for collecting the aliquots. This means that it is unlikely that there is a concentration gradient of any

significance in the solutions contained in the test tubes. It was therefore decided to employ the "pour" method in subsequent determinations, since it was the more convenient one to use.

Once again it may be seen that, except in the case of the 18μ wool at 25°C (Table 27), the concentrations after sorption are higher than those determined before the wool was placed in contact with the solutions. The positive sorption indicated here is small and the larger differences (obtained with the 16μ wool) indicate negative sorption (see Table 27). The values obtained are too erratic to be of much use as a method for estimating the sorption of such small amounts. It was realised that equilibrium had probably not been reached in these 30 minute periods, but only a comparison of data was required for the methods of collecting the aliquot and the times of sorption should have been sufficient to indicate any differences which may have existed.

In the experiments on water-saturated wool (Table 29) the degree of negative sorption indicated was consistently less than the values obtained with the unsaturated wool. This was due to the fact that no correction was made for dilution of the solution by water which was not actually adsorbed by the wool. If it is considered that the maximum regain of wool is 36% and that the regain of the conditioned wool was 15%, the 0.5 gm. sample of wool would have a dry weight of 0.435 g. and a weight at 36% moisture of 0.592 g. Since the lowest weight of the samples used after saturation was 1.236 g., the minimum weight of "unbound" water was 0.644 g. This water, being "unbound" i.e. not adsorbed by the wool, will only serve to dilute the sorption solutions and therefore give rise to a lower concentration figure. If the volume of the sorption solution in the first series

is corrected to 20.64 ml., the concentration of the blank would have been 0.0246%, compared with concentrations after sorption of 0.0250 to 0.0254% as in Table 29. (The corresponding concentration for the sample with maximum "unbound" water is 0.0242%.) This gives the same order of magnitude of negative sorption as recorded in previous experiments. These findings are in agreement with those of McLaren[34] and Weatherburn et al[140], both of whom consider it unnecessary to apply a correction for the water sorbed by the wool which was not at saturation regain. In this case it was found that applying such a correction made very little difference to the trends observed without the correction.

The only remaining explanation for the negative adsorption obtained is that the concentrations of the sorption solutions were too high and that at these high concentrations the amount of detergent sorbed was too small to be detected by the methods used. It was therefore decided to investigate the amount of sorption from dilute solutions.

9.2.2.2 Sorption by wool from dilute solutions.

Method:

0.5g. samples of cleaned, conditioned wool of 20μ diameter were used to estimate the degree of sorption from 40 ml. 0.005% Tergitol NPX. The solutions were contained in stoppered flasks which were fixed to a shaking machine, constructed to give approximately 70 oscillations per minute with a stroke of 2 inches. After the wool had been introduced into the solutions, the flasks were shaken for various periods in a constant temperature room at 20°C. On completion of the sorption period, the supernatant liquor was poured off and used for the determination. The concentrations were estimated by measuring the absorbance in a 10 mm. silica cell at 276 mμ.

Results:

The results obtained after shaking the wool samples with dilute detergent solutions at 20°C are shown in Table 30.

TABLE 30

Sorption of Tergitol NPX by wool from dilute solutions at 20°C for various periods of shaking

Time shaken (hr.)	Blank concn. (% w/v)	Concn. after sorption (% w/v)
20	0.0058	0.0125
20	0.0058	0.0215
18	0.0055	0.0105
18	0.0055	0.0135
6	0.0060	0.0075
6	0.0060	0.0066

Discussion:

Once more it was found that the concentrations after sorption were higher than those before sorption. This was especially marked in the cases where the samples were shaken for long periods. At 20 and 18 hours, the post-sorption concentrations were more than double the initial concentrations. Duplicate determinations showed that the results obtained were too erratic to be used as true measures of the small differences in concentration at say 6 hours. Several repetitions of the above work made virtually no improvement on the reproducibility of the results obtained.

The remarkable increase in concentrations of solutions after 20 hours immersion was rather unexpected, but it was thought that these large increases could be attributed to degradation products of the wool or small pieces of weathered fibre

and fine dirt particles being shaken off or removed from the fibres after swelling. These impurities are known to absorb in the same range as nonionic detergents[3] and the dirt particles would also cause an increase in absorbance as measured on the spectrophotometer. In order to test this explanation, a number of wool samples were treated in exactly the same way as above and shaken for 18 hours at 20°C in 40 ml. distilled water. No detergent was added to the solutions, but absorbance values were obtained which indicated that there was 0.0075% "detergent" present, according to the calibration curve. This is a serious limitation on the use of the spectrophotometric method for determining sorption under these conditions and it is considered that investigations of sorption at immersion times in excess of 6 hours (see Table 30) would be valueless.

In general it would seem then that the methods employed in this study for the adsorption of nonionics onto wool are not reliable enough to give absolutely consistent results. However, the work bears out the observations made by Le Compte and Creely[55], viz. that nonionic detergents are negatively sorbed by wool. These workers consider the negative sorption as being due to preferential sorption of water. This explanation does not seem likely in view of the work above on wool which was saturated with water before it was brought into contact with the solutions. Also, it is highly unlikely that the wool adsorbs no nonionic detergent at all, since this can easily be demonstrated by the fact that solutions of nonionic detergents wet out wool very rapidly whereas with water the wetting-out process is very slow. It was therefore concluded that wool adsorbs nonionic detergents in very small amounts, perhaps just sufficient to enable the wetting-out process to take place and these small concentration changes could not be measured

with much consistency using the methods outlined above.

9.2.2.3 Sorption by other substrates.

Method:

In view of the very small amounts of nonionic detergent sorbed by wool it was decided to investigate the degree of sorption onto some of the impurities present in the scouring liquors which may adsorb detergent to a greater degree than wool. A sample of sand was prepared from scouring liquor by filtering it to collect the sand, which was then shaken up with ether followed by alcohol, and allowed to dry. After it had been sifted through a 240-mesh sieve, the sand which passed through was placed in extraction thimbles and extracted in a soxhlet for 8 hours with dry diethyl ether and then for 16 hours with ethanol, dried at 105°C for 8 hours and kept in a desiccator. Dry samples of approximately 0.5 g. were weighed out for use in the subsequent sorption experiments.

The samples of sand were left in contact with 20 ml. Tergitol NPX solutions of various stated low concentrations (see Results) at constant temperatures without agitation. The supernatant liquors were used for the concentration determinations by absorbance measurements in a 40 mm. infrasil cell. Considerable difficulty was experienced in obtaining a clear supernatant liquor from the above experiments, but centrifugation was found to effect considerable improvement in the appearance of the supernatant liquors.

In view of the problem encountered in preparing a clear supernatant solution from the fine sand sorptions, it was decided to use sea-sand which was much coarser than the dust on wool in order to obtain more reliable results. A lot of sea-sand was sieved through a 90 mesh sieve and extracted as follows, using a

soxhlet: 8 hours with dry diethyl ether and ~~for~~ 16 hours with water. Since this sand had a smaller surface area per unit weight, smaller amounts of sorption were expected.

Approximately 0.5 g. of dry sea-sand was weighed out for each determination and left in contact with 20 ml. of solution of the appropriate concentration for 4 hours at 35°C. The supernatant liquors were used for the concentration determination in a 40 mm. infrasil cell. This procedure was repeated using approximately 0.5 g. samples of sea-sand in 20 ml. detergent solution at 35°C for 2½ hours. The supernatant liquors were used for the estimation of the detergent concentration. Several blanks were included where 20 ml. portions of detergent solution alone were kept at 35°C for 2½ hours.

Three further experiments were carried out in order to establish whether the degree of sorption onto 240 mesh-and sea-sand is influenced by mechanical agitation or the time of immersion. The samples were shaken for 20, 18 and 6 hours on the mechanical shaker described above at 20°C.

Results:

The results obtained after the supernatant liquors from the 240 mesh sand experiments had been centrifuged are shown in Table 31. The behaviour of very dilute solutions of detergent in the presence of fine sand was borne out by several duplications. No actual peak could be observed at the wavelength used.

In the case of sea-sand, the peak at 276mμ persisted down to concentrations of 0.001% Tergitol NPX.

TABLE 31

Sorption of Tergitol NPX by 240 mesh sand after 2 hours (no agitation) at 35°C

(Measurements in 40 mm infrasil cell, sorbent:liquor ratio 1:40)

Weight sand (grams)	Blank concn. (% w/v)	Concn. after sorption (% w/v)
0.5016	0.008	0.00815
0.5005	0.005	0.0077
0.5019	0.002	No peak
0.5010	0.001	No peak

TABLE 32

Sorption of Tergitol NPX by 90 mesh sea-sand after 4 hours (no agitation) at 35°C

(Measurements on 40 mm. infrasil cell, sorbent:liquor ratio 1:40)

Weight sand (grams)	Blank concn. (% w/v)	Concn. after sorption (% w/v)
0.5041	0.008	0.0087
0.5014	0.005	0.0071
0.5061	0.002	0.0033
0.5021	0.001	0.0028

The results obtained when the blanks were subjected to the same treatment as the samples themselves are shown in Table 33.

TABLE 33

Sorption of Tergitol NPX by 90 mesh sea-sand after 2½ hours (no agitation) at 35°C

(Measurements in 40 mm. infrasil cell, sorbent:liquor ratio 1:40)

Weight sand (grams)	Blank concn. (% w/v)	Concn. after sorption (% w/v)
0.5009	0.0088	0.00897
0.5008	0.00483	0.00565
0.5054	0.00198	0.00255
0.5008	0.00193	0.00193

The results of the sorption measurements for long immersion times (with mechanical agitation of the sample) measured on both types of sand are given in Table 34.

TABLE 34

Sorption of Tergitol NPX by 90 and 240 mesh sand at various times of immersion at 20°C

(Measurements in 40 mm. infrasil cell, sorbent:liquor ratio 1:80)

Agitation time (hrs.)	Weight sand (gm.)	Size of sand particles (mesh)	Blank conc. (% w/v)	Concn. after sorption (% w/v)
20	0.5000	240	0.0059	0.008
20	0.5040	240	0.0059	0.0083
20	0.5060	90	0.0059	0.0072
20	0.5040	90	0.0059	0.008
18	0.5000	240	0.0055	0.010
18	0.5000	90	0.0055	0.0075
6	0.5063	240	0.0060	0.0065
6	0.5064	240	0.0060	0.0066
6	0.5053	90	0.0060	0.0060
6	0.5041	90	0.0060	0.0060

Discussion:

Negative sorption was once again recorded in all cases. It may be assumed that in some cases at least, equilibrium had definitely been established and that the substrates had been agitated sufficiently in order to expose their total surface areas to the solutions from which the sorptions were measured. It is not possible that the work could have been carried out at the points where minimum adsorption takes place (if indeed the nonionic detergents should display the same sorption characteristics as the ionic types), since a very wide range of concentrations was investigated.

The determinations with the 240 mesh sand were complicated by the fact that the very fine sand particles remained in suspension, even when prolonged standing was allowed for settling the sand, and obscured the peaks which were measured. This problem was solved eventually by centrifuging the supernatant liquor for 2 minutes at 10,000 r.p.m. Even then, extreme care had to be exercised when decanting the supernatant liquor from the centrifuge tube since the smallest amount of agitation caused the sediment to become suspended once more. Fortunately it was quite easy to establish whether this procedure had been carried out with due care since the presence of very small amounts of suspended dust caused misshapen peaks or no peaks at all to be recorded at extremely low detergent concentrations (0.001 to 0.002% w/v) as shown in Table 31. This was probably due to the obscuring effect of very small amounts of suspended dust in solutions, the blanks of which showed only very little absorbance themselves. The experimental procedure in the case of the sea-sand was simplified considerably by the fact that the coarser sand showed no tendency to remain in suspension, and no difficulty was experienced in determining the detergent concentrations at the lowest values used. (See Table 32).

It was thought that evaporation of water might have been a contributory cause of the higher post-sorption concentrations. The results in Table 33 show that when the blanks are given the same treatment as the samples, there is no difference in the results recorded. All subsequent blanks were treated in this manner as a precautionary measure, even though it had been shown to make very little difference to the results obtained.

It was found that the 240 mesh sand gave consistently

higher negative sorptions than did the 90 mesh sand (Table 34). This may have been due to incomplete removal of the fine dust in the case of the 240 mesh sand.

9.2.2.4 The effect of electrolytes (builders) on sorption by wool.

Method:

Before any sorption measurements were carried out, the effect of the presence of electrolytes on the determination of non-ionic detergents was investigated by adding various concentrations of builder to a solution of nonionic detergent in distilled water. Three electrolytes were used, viz. NaCl, Na_2CO_3 and Na_2SO_4 at concentrations approaching saturation at 20°C. The absorbance of the samples was measured in a 10 mm. silica cell at 276.3mμ.

The sorption experiments were then carried out by shaking up 0.5 g. samples of wool with 40 ml. of solutions containing electrolytes as well as nonionic detergent for various periods at 20°C. The effect of ageing of the solutions was investigated by leaving samples for two days before they were measured for a second time.

Results:

The effect of electrolytes on the determination of nonionic detergents is shown in Table 35.

TABLE 35

Effect of added electrolytes on the determination of concentration of nonionic detergents

Solution	Blank concn. (% w/v)	Conc. found (% w/v)	"Increase" in concn. (% w/v)
0.005% Tergitol in 2 M NaCl	0.0046	0.007	0.0024
0.005% Tergitol in M Na_2CO_3	0.0046	no peak	-
0.005% Tergitol in M/2 Na_2SO_4	0.0046	0.0063	0.0017

The effect of the presence of electrolytes on the sorption of nonionic detergents by wool is shown in Table 36. The samples were agitated for the periods stated.

TABLE 36

Effect of electrolytes on the sorption of nonionic detergents at 20°C
Wool:liquor ratio 1:80

Solution	Agitation time (hr.)	Blank concn. (% w/v)	Conc. after sorption (% w/v)
$M/_4$ Na_2SO_4	20	0.0059	0.0396
$M/_2$ Na_2CO_3	20	0.0059	No peak high absorbance
M NaCl	20	0.0059	0.0466
$M/_4$ Na_2SO_4	18	0.0055	0.009
$M/_2$ Na_2CO_3	18	0.0055	No peak
M NaCl	18	0.0055	0.0075
$M/_4$ Na_2SO_4	6	0.0060	0.0070
M NaCl	6	0.0060	0.0070
$M/_2$ Na_2CO_3	6	0.0060	No peak low absorbance

Discussion:

There is a significant absorption contribution from the electrolyte solutions (Table 35), and the results in Table 36 should be viewed with a certain amount of caution. High concentrations of electrolyte were investigated, since McLaren[34] was able to measure the sorption of nonionics by wool under similar conditions. Large negative sorptions are indicated, even when the "background sorption" of the electrolyte solution is subtracted (assuming that the effect is additive), and the increases in concentration are larger than any others recorded

in the course of this study, especially those obtained after 20 hours agitation. The negative sorption is considerably less marked at 6 hours. This can be explained in terms of the effect of long immersion and agitation times (see 9.2.2.2, where it was found that a considerable absorbance contribution was obtained from the wool itself, the contribution decreasing with the time of immersion).

From the results obtained with Na_2CO_3, it will be seen that no peak could be observed in any of the experiments. Also, at 20 hours immersion, a high absorbance was measured, whereas at 6 hours the absorbance measured was quite low. This seems to indicate that after long immersion times, some degradation of the protein by the Na_2CO_3 has taken place. These degradation products themselves are also expected to absorb in the range of wavelengths used[3].

10. DETERMINATION OF DETERGENT INACTIVATION BY ADDED IMPURITIES.

10.1 Introduction.

In the direct sorption measurements carried out in the previous chapter, the results consistently indicated negative adsorption of nonionic detergents by all substrates studied. It was then decided to attempt to measure adsorption by an indirect method in which the amount of sorption or detergent inactivation could be related to a surface activity phenomenon such as detergent efficiency. It was concluded from the detergent consumption figures obtained in the backflow study (Chapter 4) that the presence of high concentrations of solids in the liquors definitely caused some kind of inactivation of the detergents present, be it by sorption onto the impurities, emulsification of grease, etc.

It was thought that if a number of uniform samples of raw wool were washed under exactly identical mechanical and chemical conditions, but with changes in the percentage of total solids present in the liquors, the detergent efficiency (measured in terms of residual grease) would be an indication of the amount of detergent inactivated or sorbed by the wool or other impurities present in the scouring liquor. This would also be an indication of the amount of detergent available for scouring.

10.2 Apparatus.

The apparatus required for the washing procedures had to be able to scour a 2 g. sample of raw wool to an acceptable residual grease content (0.6 to 1.0%) within a reasonable time at a detergent concentration not exceeding 0.05% w/v, which is comparable with the concentrations used in wool scouring.

Preliminary investigations were carried out on an automatic

pumping device used by Bamford[141] with a high-grade stainless steel metal tube and a plunger which is a fairly close fit[29]. The plunger was driven through a 40:1 reduction gear which gave 20 strokes per minute. Preliminary investigations gave residual grease values of higher than 1%. It was decided to replace the 40:1 reduction gear by one with a 25:1 ratio. Under these conditions a 0.05% Lissapol NX solution gave a residual grease content of 0.77% after a 15 minute wash and a 3 minute rinse in distilled water at 60°C, which was considered to be satisfactory.

10.3 Method.

The washing procedures used were carried out under standard conditions as follows:- The wool samples were prepared by taking a sample from one of the scouring lots. This lot was zoned and each zone opened separately on a pair of hand-cards and then blended together. The opened sample was then rezoned and the above procedure repeated. The large sample was then conditioned for two days before the individual 2 g. samples were weighed out. The sample of wool obtained in this way gave a reasonably constant grease content viz. 15.56, 15.07, 15.00 and 15.04%, an average of 15.17%.

The solutions containing the contaminating solids were prepared from raw wool which was drawn from the same uniformly blended scouring lot. The wool was placed in hot water (contact with detergents was carefully avoided at all stages) to soak and was squeezed to wet it more thoroughly. The wool was then removed and the solutions poured through a fairly fine sieve to remove the larger pieces of vegetable matter and small lumps of wool which proved troublesome when portions of the solution were pipetted out. The solutions contained approximately 5 to 7% total

solids at this stage and were further concentrated to approximately 10 to 12% total solids by evaporation. It was found that the solutions did not keep very well at room temperatures and new solutions had to be made up every second day. The solutions produced in this way were fairly similar to those which are obtained from scouring liquors in that a solution which contained 10.32% total solids was found to consist of 2.59% grease (ether-extractable matter) giving a solids:grease ratio of 3.98. The scouring effluent in the backflow study (see Chapter 4) gave a solids:grease ratio of 2.9.

A wool:liquor ratio of 1:30 was employed throughout the experiments and the detergent concentration was kept constant at 0.05%. Aliquots were taken from the concentrated solutions and added to the tube in order to make up 60 ml. of solution containing the required amount of detergent and percentage of solids.

The samples were clamped to the piston as described elsewhere[141]. The tube was kept in a thermostat at 60°C and 15 minutes were allowed for the liquor to reach the temperature of the bath. The distilled water which had to be added was kept at 60°C in a flask which was also immersed in the bath. The samples were scoured for 15 minutes at 30 strokes per minute (25:1 reduction gear) and removed from the tube. The contents of the tube were poured out, the tube rinsed and 60 ml. of distilled water at 60°C added to the tube. The piston (with sample) was replaced and the sample rinsed under the same conditions for 3 minutes. After rinsing, the samples were removed from the piston, opened by hand and dried for 20 minutes at 65°C in a Rapid Regain Tester. The residual grease was then determined by the column and tray method[52], and the results expressed as percentage grease on the original conditioned weight of the sample (2 g.).

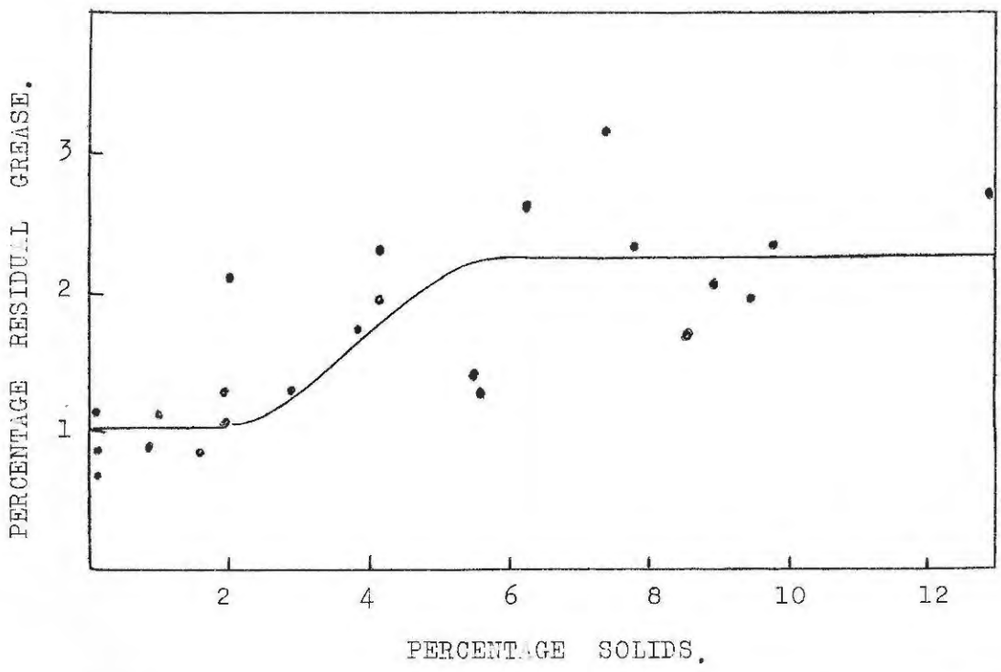


Fig. 28. Effect of added solids on detergent efficiency of Lissapol NX.

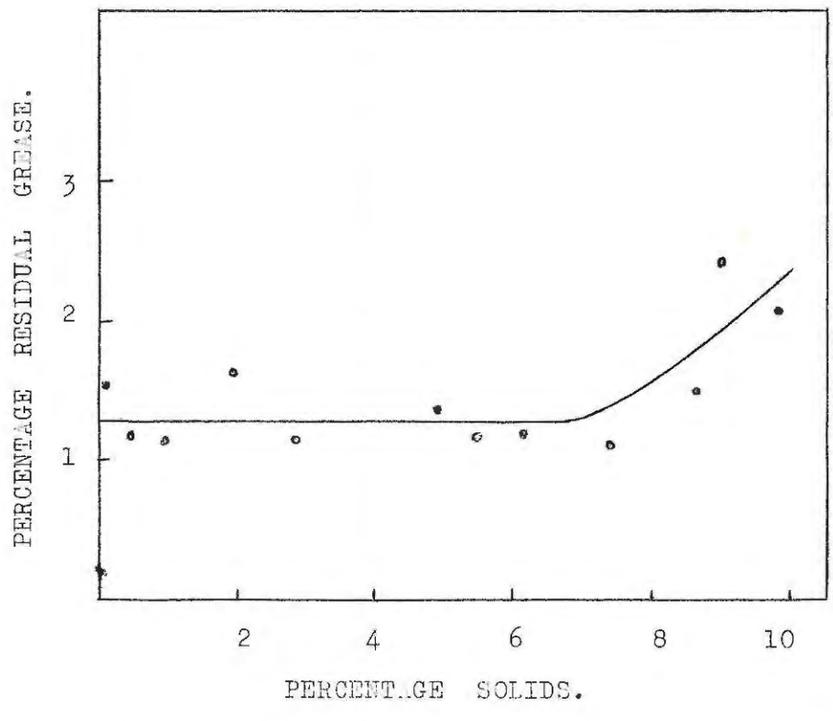


Fig. 29. Effect of added solids on detergent efficiency of Fluidol W100.

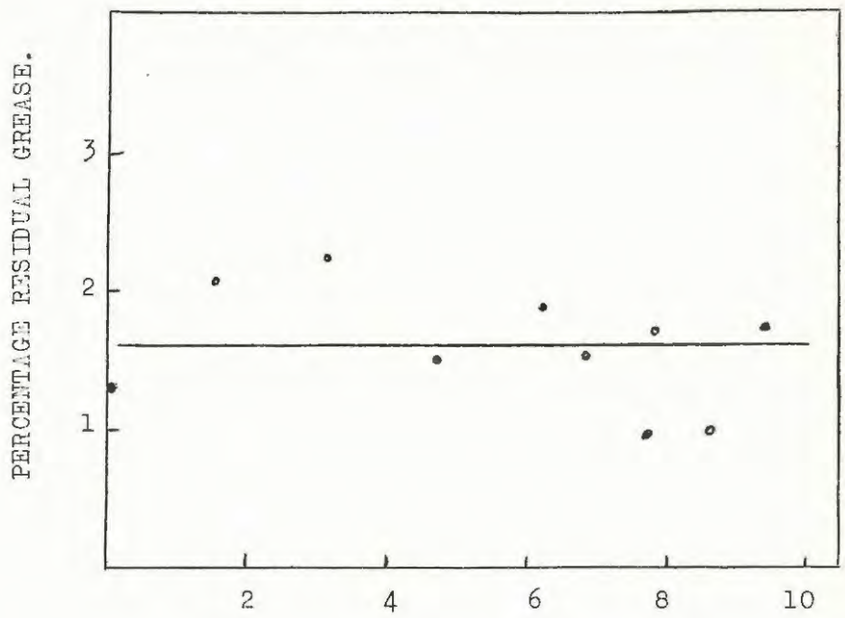


Fig. 30. Effect of added solids on detergent efficiency of Triton N100.

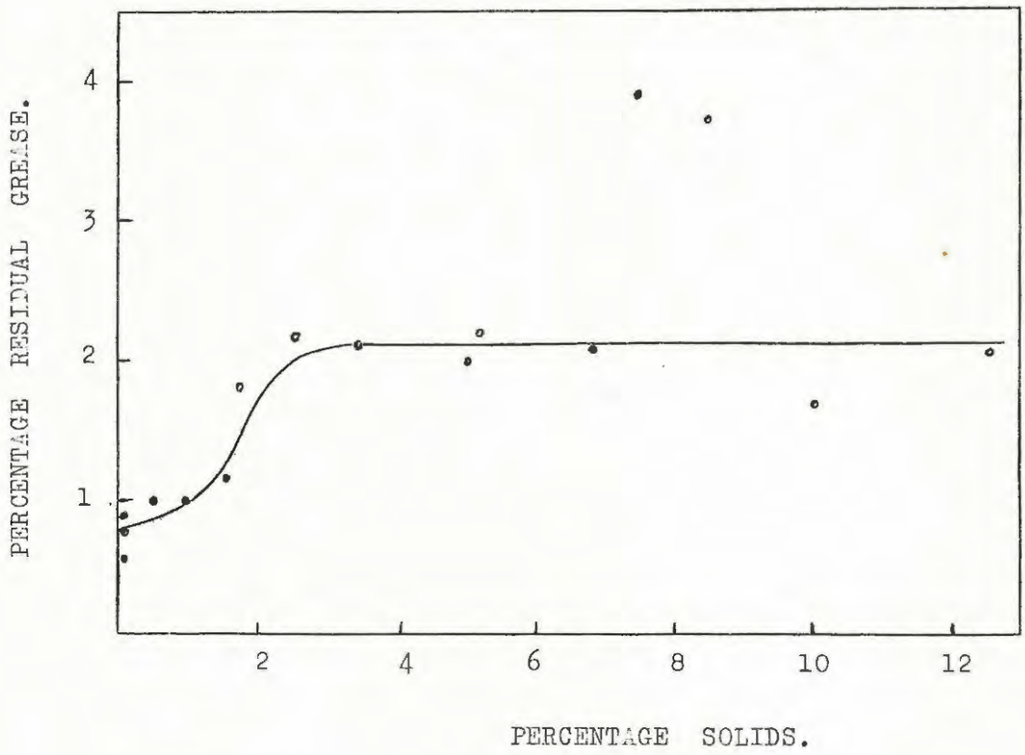


Fig. 31. Effect of added solids on detergent efficiency of Tergitol 12P9.

A range of solids concentration from 0 to 12% was investigated for four different nonionic detergents.

10.4 Results.

The results obtained for the different detergents are shown in Table 37 and Figs. 28 to 31. Detergent concentrations were 0.05% w/v throughout.

10.5 Discussion.

From Fig. 28 it will be seen that the detergent efficiency of Lissapol NX falls off gradually over a fairly wide range of solids concentration, from approximately 2 to 6%. In the case of Fluidol W100 (Fig. 29), the drop in detergency is much more abrupt and commences at approximately 7% total solids, whereas the efficiency of Triton N100 is not affected markedly by changes in total solids concentration from 0 to 10%. For Tergitol 12P9 (Fig. 31) the decrease in detergency sets in at approximately 1% total solids. There are two points on the Tergitol 12P9 plot which are extraordinarily high; these were caused by lubricating oil which had run down the shaft of the piston onto the sample, and they were ignored in drawing the curve.

After the decrease in detergency has taken place, the residual grease values show only small increases and stay more or less constant with further addition of solids to the liquors. According to Wolfrom and Nuessle[27], the rate of operation of a pumping machine similar to the one used has a considerable effect on the cleaning efficiency. This was confirmed in the preliminary investigations using the slower reduction gear where considerably higher grease contents were found for the same time of agitation and detergent concentration as were used in the main study. It is

TABLE 37

Washing experiments with four different nonionic detergents

a) Lissapol NX

Concn. solids (g./100 ml)	Residual grease (%)	Concn. solids (g./100 ml)	Residual grease (%)
0	0.87	5.16	2.01
0	1.16	5.50	1.38
0	0.67	5.54	1.26
0.82	0.88	6.28	2.63
0.97	1.11	7.37	3.18
1.56	0.84	7.80	2.33
1.93	1.31	8.60	1.71
2.05	2.14	8.95	2.06
2.89	1.29	9.46	1.97
3.86	1.71	9.82	2.34
4.11	2.31	12.95	2.71
4.11	1.96		

b) Fluidol W100

Concn. solids (g./100 ml)	Residual grease (%)	Concn. solids (g./100 ml)	Residual grease (%)
0	1.54	5.50	1.17
0.49	1.14	6.14	1.17
0.97	1.12	7.37	1.09
1.93	1.63	8.60	1.49
2.89	1.21	8.95	2.44
4.90	1.35	9.82	2.08

c) Triton N100

Concn. solids (g./100 ml)	Residual grease (%)	Concn. solids (g./100 ml)	Residual grease (%)
0	1.30	6.88	1.52
1.57	2.08	7.74	0.94
3.14	2.23	7.85	1.68
4.71	1.50	8.60	0.98
6.28	1.88	9.46	1.72

d) Tergitol 12P9

Concn. solids (g./100 ml)	Residual grease (%)	Concn. solids (g./100 ml)	Residual grease (%)
0	0.57	3.44	2.07
0	0.88	5.02	1.98
0	0.74	5.16	2.17
0.50	1.00	6.88	2.06
1.00	1.00	7.54	3.92
1.50	1.15	8.60	3.71
1.72	1.82	10.04	1.63
2.51	2.15	12.56	2.01

thought likely that the pumping machine, due to its vigorous mechanical action, together with the elevated temperatures (60°C) used, might be able to scour the plugs of wool to a 3% residual grease level, even when very little detergent was left in a form suitable for scouring.

The decreases in detergency indicated must be related to the amount of detergent inactivated by the presence of the contaminants in the liquors, be it by adsorption, emulsification, etc. It will be seen that the degree of decrease in detergency is different for all four detergents investigated and that the decreases set in at different solids concentrations. Confirmation of these results was found in the pilot-plant study on the effect of backflow (Chapter 4) where the two detergents used were found to react very differently under varying backflow conditions. The main effect of differing rates of backflow is in changing the concentration of total solids in the scouring bowls.

Tergitol 12P9 is the most hydrophobic detergent of the four which were tested (it has a cloud point of only 18°C), which means that it has a rather short hydrophilic ethylene oxide chain. The results obtained in this case (Fig. 31) indicate that detergent inactivation (i.e. adsorption, etc.) set in at a very low solids concentration. This is in agreement with the results of several investigators who have reported that the degree of sorption of nonionic detergents increases with decreasing ethylene oxide chain length[54,136,137], since the adsorptional cross-sectional area of the detergent molecule increases with increasing chain lengths. This points to adsorption as the main factor contributing to detergent inactivation.

If the results for the three detergents which showed a decrease in detergency with varying solids concentrations were interpreted in terms of backflow requirements, the rates of backflow to be used for minimum detergent consumption would increase in the following order for the different detergents: Fluidol W100, Lissapol NX and Tergitol 12P9. This conclusion was confirmed in the first two cases by the pilot-plant investigation of the effect of the rate of backflow (Chapter 4) in which it was found that the minimum detergent consumption for Fluidol W100 occurred at 50% backflow (approximately 7% total solids) and that the detergent consumption for Lissapol NX had not yet reached the minimum at 116% backflow (approximately 3% total solids).

10.6 Conclusion.

The four detergents studied showed different reactions to increases in the total solids content of the scouring liquors. The decreases in detergency found were attributed to the inactivation of detergent by the contaminants added. It was assumed that the main inactivating effect operating was adsorption, since the detergent with the smallest ethylene oxide mole ratio, which was expected to have the greatest tendency to sorption, showed a decrease in detergency even at very low solids concentration.

SUMMARY AND CONCLUSIONS.

A. Mechanical Action.

Sixty-four individual lots of raw wool were scoured in order to investigate all the possible permutations arising from four different settings of three factors, viz. rake speed, roller speed and rate of feeding.

Within the limits of the experimental conditions, an increase in the squeeze-roller speeds and the rate of feed caused a decrease in detergent consumption, whereas an increase in the rake speed caused an increase in detergent consumption.

Measurements of the average fibre length after combing indicated no significant differences resulting from the various scouring treatments. The smallest number of neps was produced by the lots which were scoured at the highest rate of feed.

B. Influence of backflow.

The effect of different rates of backflow during the scouring of raw wool was investigated from the point of view of detergent efficiency and effect on build-up of solids in the scouring bowls.

A new rapid method for the estimation of the concentration of suspended solids is described. The equilibrium concentration of total solids in the first bowl was found to be inversely proportional to the rate of backflow employed and a fairly constant relationship was obtained between the equilibrium total solids content of the first and second bowls.

The two detergents used showed widely divergent reactions to variations in the rate of backflow, and they required different rates of backflow for minimum detergent consumption.

C. Influence of temperature.

The effect of temperature on the scouring of raw wool was investigated by scouring several lots of wool under varying conditions of temperature in the first and second scouring bowls while all other temperatures and conditions were kept constant.

An increase in temperature in either of the first two bowls caused a decrease in detergent consumption. This effect was very marked at the lower temperatures, but diminished considerably in the higher regions. The first bowl temperature was found to be the dominant factor in determining the detergent consumption when a nonionic detergent was being used.

From the response surfaces estimated for detergent consumption on temperature, it was concluded that a point of minimum detergent consumption existed for the nonionic detergent, but no such point could be found for soap.

D. Comparison of detergents.

Several detergents were compared for scouring efficiency using two types of wool. The scouring lots were compared under fixed conditions, and the detergent consumption figures were converted to costs on the basis of quotations for 2,000 lb. lots, f.o.r. Port Elizabeth.

Nonionic detergents could be used at considerably less cost than soap when scouring low-yielding Lox, but for a higher yielding fleece-wool, soap became more competitive economically.

When pairs of nonionics which were derived from the same hydrophobe were compared, it was observed that the detergent which had a cloud point lower than the scouring temperatures operated more efficiently than one whose cloud point was higher than the temperatures of the scouring bowls.

E. Effect of detergency builders.

The optimum total addition of detergency builders to the first and second bowls was determined for three builders, viz. sodium sulphate, sodium chloride and sodium carbonate. These optimum total quantities were used as a basis for investigating the effect of varying the ratio of additions of builders to the first and second bowls. Combinations of builders were also studied.

The order of efficiency of the builders for nonionic detergents was found to be: sodium carbonate, sodium chloride and sodium sulphate. For soap, sodium carbonate was again the most efficient builder and the effects of sodium sulphate and sodium chloride were very similar. Detergent consumption was found to decrease sharply on increasing additions of builders in the lower concentration ranges. This effect became considerably less marked in the higher ranges.

When the total additions were kept constant, the ratio of the amounts of builders added to the first and to the second bowls respectively did not appear to have any marked influence on the detergent consumption.

From a paired comparison experiment conducted on samples scoured under extreme conditions of builder additions it was concluded that the use of excessive amounts of sodium carbonate in the scouring liquors had a significant discolouring effect on the scoured wool.

F. Estimation of nonionic detergents.

Two gravimetric methods were investigated, viz. precipitation with phosphomolybdic acid and with phosphotungstic acid. Both methods were found to be sufficiently accurate when applied to

pure aqueous solutions of nonionic detergents. The presence of degraded protein material caused considerable interference in that it was precipitated together with the detergent. A nonionic detergent with a low cloud point gave very erratic results which can probably be ascribed to concentration gradients in the solution.

A spectrophotometric method was investigated in which the absorbance of the detergent solution was measured at 276 mμ. This method was admirably suited to the determination of nonionic detergents in pure aqueous solutions, although the accuracy of the method started falling off in the very low concentration ranges.

An indirect polarographic method was also investigated in which the excess phosphotungstic acid from the above gravimetric procedure was determined. Reasonably accurate calibration curves were obtained for pure phosphotungstic acid solutions, but when the method was applied to the mother liquor from the precipitation mixture, erratic results were obtained. These erratic results were probably due to adsorption of phosphotungstic acid by the precipitate formed, making the amount of phosphotungstic acid left in the mother liquor an unreliable gauge of the amount of nonionic detergent precipitated.

In general, it seems that the methods investigated would be unsuitable for the determination of nonionic detergents in any medium other than pure aqueous solutions.

G. Sorption of nonionic detergents.

The sorption of nonionic detergents from aqueous solutions was measured for various types of substrate (wool and sand of different grades). Sorption by wool was studied using relatively concentrated as well as dilute solutions. The effect of electrolytes on the sorption of nonionic detergents by wool was also investigated.

Practically all the results obtained indicated negative sorption since the concentrations of the solutions after sorption were higher than before. The factors which may have been responsible for this phenomenon (preferential sorption of water, evaporation from solutions and effect of extraneous material) were investigated, but no reasonable explanation could be found.

H. Detergent inactivation.

A number of uniform samples of raw wool were scoured under identical mechanical and chemical conditions with changes in the percentage of total solids present in the liquors.

The detergent efficiency (measured in terms of residual grease) was taken to be related to inactivation of detergent by the contaminants added. The four detergents studied showed different reactions to increases in the total solids concentration which were confirmed by results obtained in the backflow study. It was assumed that adsorption was the main inactivating effect, since the detergent with the smallest ethylene oxide mole ratio, which would be expected to have the greatest tendency to sorption, showed a marked decrease in detergent efficiency even at very low concentrations of solids.

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PUBLICATION OF PRESENT WORK.

A. The following papers have been accepted for publication by the Journal of the Textile Institute and will be printed shortly.

   a) The effect of Mechanical Action on the Scouring of Raw Wool.

   b) The effect of Backflow on the Scouring of Raw Wool.

B. Papers on the following subjects have been submitted for publication to the Journal of the Textile Institute.

   a) The effect of Temperature on the Scouring of Raw Wool.

   b) Comparison of Detergents for Raw Wool Scouring.

   c) The effect of Detergency Builders on the Scouring of Raw Wool.