

INDUSTRIAL SECTION

The Chemistry of Detergents

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A DETERGENT is broadly defined as "a washing or cleansing agent such as soap, scouring compositions, etc." and detergency as washing or cleansing. The detergent action of the alkalis and of certain of their salts such as the silicates and phosphates is well known and, more recently, the detergent action of colloidal clays has been recognized. Soaps were the earliest organic detergents and, although numerous synthetic organic detergents with certain advantages have been evolved, the soaps have by no means been abandoned in detergent practice on account of their fundamentally valuable properties and their cheapness. In fact the synthetic detergents are in general not as satisfactory as soap for the usual fabrics, so long as the water is soft. The detergent action of alkalis may be partly attributed to the soaps formed from the saponifiable matter present in the material being deterged, and the action of colloidal clays to their adsorptive capacity. Used in conjunction with soap, the addition of colloidal clay increases lathering power, makes a firmer and more powerful lather, and absorbs and neutralizes free alkali.¹ The washing of textiles, hair or skin with a detergent composition containing a sulphonated product of the Igepon type and a colloidal clay like Bentonite has been claimed (Fr. Pat. 820,661).

Much attention has been directed in recent years to the mechanism of detergent action. Partly as a result of the truer insight now available into the many factors governing detergent action and of the more stringent necessities of modern textile processing with regard to the delicate nature and variety of the fabrics and to the importance of the time factor in production, it has been possible for the synthetic organic chemist to arrive at substances which are efficient detergents and which have in addition to their detergent action a number of desirable properties which enable them to be used under widely varying conditions.

In a recent symposium² organised by the International Society of Leather Trades

Chemists a very comprehensive and illuminating survey has been made of the theoretical aspects of wetting and detergency. While the newer concepts of the physics and chemistry of surfaces, due to Freundlich, Hardy, Langmuir, Adam and Rideal, have led to better understanding of the arrangement of detergents and emulsifying agents at interfaces and of the molecular forces which play a part in the gradual accomplishment of the ultimate result of detergency, this has simultaneously complicated the work of the manufacturer of textile auxiliary agents, since the processor has begun to realise that the detergent for a given purpose and set of conditions may be entirely unsuitable under other circumstances. To the synthetic organic chemist, however, the broadening of the theoretical bases of detergent action and the quantitative considerations and methods that have emerged in consequence have meant the opening up of a new and extensive field of research.

A wetting agent need not *per se* be a detergent, but in general wetting or penetrating power towards textile fibres is a desideratum in a detergent. Whatever may be the theory finally adopted regarding the mechanism of detergent action, it is as necessary for a detergent as for a dyeing process that the reagent must initially come into intimate contact with the surface of the textile material. Adsorption should then take place, the detergent having a greater attraction for the surface to be deterged than the grease, oil or "dirt" which is to be removed. Rideal³ has suggested that detergents, like dyes, are first adsorbed on the outer surface of the fabric and then migrate into the interior accessible surface. The oily or greasy film is then loosened on account of its displacement by the detergent, the oil collecting into comparatively large globules.³ Dependent on the agitation to which the scouring liquor and the deterged surface are submitted and the emulsifying power of the detergent or of a second added substance, an emulsion of the oil may be formed or the

oil may be removed by a process of flotation. The last factor which determines the detergent efficiency as measured by any practical test, such as whiteness or wax content, would be the prevention of redeposition of the oil or dirt on the surface of the fabric; here presumably the protective colloidal power of the detergent is concerned. Rideal² considers that the polar head of a detergent may also fulfil a definite chemical function in addition to the more usually recognized physical function of rendering a hydrophobic surface hydrophilic in character; loose molecular complexes may be formed between the polar heads of the detergents and the alcoholic groups in the oil or grease or the keto-imide groups in protein "dirt". The hypothesis would be limited by the nature of the dirt and by the availability of detergents which do not possess a polar head or ionising group.

The two stages of adsorption at the interface and migration into the intermicellar spaces of a fibre may be difficult to demonstrate experimentally in the case of the common reagents not susceptible to identification by colour reactions. Anacardic acid, which is a constituent of cashew nut shell oil and, being a derivative of salicylic acid, gives an intense coloration with ferric chloride, should prove useful for studies in the mechanism of detergent action. Carrying a pentadecadienyl residue *ortho* to the phenolic hydroxyl, the sodium salt of the acid has marked wetting power and its detergent properties are under examination.

The factors involved in detergent action are so complicated that the problem of measuring the detergent efficiency of a given substance is beset with even more difficulties than the measurement of wetting power;⁴ on the other hand a quantitative assay of detergency is fundamental to a study of its relation to chemical constitution. The physical properties usually determined, such as surface tension or interfacial tension in terms of the drop number, wetting intensities, contact angles, etc., are not related in any known manner to actual detergent power.⁵ Zakarias⁶ regards protective colloidal action as the essential criterion of detergent efficiency, but it is common knowledge that the two do not necessarily go hand in hand, judging detergent power by any practical test. In a discussion of soluble soap, insoluble soaps and synthetic detergents, Crowe⁷ has briefly outlined theories

of detergency and has referred to the dependence of the choice of a detergent for a given process on the process itself and on the composite quality of the detergent, rather than on the consideration of individual factors. The sulphonated oils (Turkey Red oil, Prestabit oil, etc.), whatever the degree of sulphonation may be, are devoid of detergent power in spite of possessing other valuable properties such as wetting, dispersing and emulsifying power. This contrast in properties, pointing to the more specific requirements in an organic compound to develop detergency, is further exemplified by the alkylnaphthalene sulphonic acids (Nekal BX, Perminol W, Oranit), which are powerful wetting agents, but not detergents. The distinct aspects of wetting and solvent action involved in detergency are recognized by the use of non-detergent wetting agents like the Nekals in conjunction with chlorinated and other solvents. Likewise it has been suggested that the detergent properties of the sulphated alcohols are improved by admixture with unsulphated alcohols; the contrary suggestion that the presence of unchanged fatty alcohol acts detrimentally on the detergent power of the sulphate has also been made.⁸ The explanation probably lies in the relative amounts of the unsulphated alcohol present. A direct measurement⁹ employing washing or kier boiling tests is essential. From the practical point of view the analysis of the factors underlying detergent action would indicate that the nature of the material to be deterged and the nature of the "dirt" to be removed are both to be taken into account in assessing the efficiency of a detergent; the conditions with regard to temperature, pH, etc., must also be closely defined. Confining oneself to a comparative study of the detergent efficiency of members of a homologous series, the determination of an individual property, such as interfacial tension or foam number, may give useful indications. Thus Götte¹⁰ found that in the series $C_nH_{2n+1}-O-SO_3Na$ the maximum "washing effectiveness" at 60° corresponded to the maximum Steipel foam number. The alkaline washing effectiveness in soft water was a maximum at C_{16} , but it was observed that for every temperature and degree of water hardness there was an optimum alkyl sulphate. The maximum washing efficiency was displaced in the direction of increasing chain length with increase in temperature and in the hardness of the water.

In assessing the value of a detergent to be employed in textile processing, a factor of great importance is its stability to the reagents involved, particularly acids and alkalis. Resistance to hard water or ability to disperse calcium soaps¹¹ is another desirable characteristic. Used in soft water, soap is an excellent detergent and its survival, in the face of strenuous competition from a host of synthetic auxiliary agents, as still the most widely employed detergent is ample evidence of its value in this regard. Its chief drawback is its instability to acid and to metallic ions, such as magnesium and calcium. For the scouring of cotton materials, the reagent needs to be stable to alkali; substances such as Igepon A, Avirol and Aerosol OT, which are esters hydrolysable by boiling alkali, but have otherwise useful properties as wetting and emulsifying agents, would fail to function in a kier boiling operation.

While synthetic detergents are usually built on a soap model consisting of a hydrophobic and a hydrophilic half, quantitative examination of a series of detergents would readily show that the structural features that are favourable to the conferment of detergent power may to some extent be defined, but it is no more possible than in the case of the relation between chemical constitution and physiological action to arrive at forecasts of the constitution of substances with maximum detergent power. The precise degree of the detergent power is a specific property of a particular compound, depending on the interplay of forces between the various groups or atoms in the molecule.

On the basis of our present knowledge of the probable stages involved in detergency, and as a guide to synthetic effort, an ideal detergent may be postulated to have the following properties in the optimum degree: (1) affinity for the surface to be deterged; (2) solubilising or peptising power towards oil or grease; and (3) protective colloidal action. Other favourable factors are solubility in water and ability to function under adverse conditions, *e.g.*, in hard water and at wide variations of temperature, pressure, acidity and alkalinity. Solubility in water is not intrinsically necessary in a detergent, since the example of adsorbent clays as detergents has been quoted; but water-insoluble detergents can only function where the agitation employed is such that access of the detergent to every part of the deterged

surface is ensured throughout the process; in any textile operation involving detergents, as in kier boiling, the fibrous material would act as a filtering medium and the detergent would be rapidly put out of action. A certain minimum solubility in water is, therefore, essential in a detergent for textile purposes.

Considering the three requisites in a detergent outlined above, fulfilment of the first would be dependent on the nature of the fibre, and the constitutional characteristics of a detergent for cotton and the cellulosic fibres would differ from those of a detergent for wool and the protein fibres. Experiments in this laboratory have naturally been concerned almost exclusively with cotton and, although they are still in the early exploratory stages, it has been possible to obtain some indication of the dependence of detergent power on the affinity of the reagent for the fibre or, as it may be termed by analogy with dyestuffs, on its substantivity. The nature of substantivity, which will be discussed elsewhere in more detail with reference to synthetical experiments in the Naphtol AS group, is still obscure. In the case of the polypeptide fibres containing free and potential amino and carboxyl groups, the explanation of their behaviour towards dyes and other electrolytes on organic, colloidal or electrochemical grounds can all be correlated. The nature of cellulose largely rules out the possibility of chemical combination; we are, however, now aware that the cellulose molecule is not as completely inert as usually conceived and the hypotheses, confirmed by X-ray evidence, of the constitution of cellulose as long chains of anhydroglucose units held together laterally by residual forces and of the micellar structure of the cotton fibre, are adequate to account for the behaviour of cellulose in processes such as mercerisation and towards dyes and other reagents for which it exhibits affinity. The dyestuff chemist has accumulated data regarding the structural features of an organic compound which are favourable to substantivity to the cotton fibre. Our knowledge of the subject, due mainly to Ruggli,¹² may be briefly set down as follows, in so far as it is relevant to the present purpose. (1) The substantivity of symmetrically constituted azo dyes has been explained by Meyer as due to the straight chains of the cellulose molecules attaching themselves, probably by means of covalencies,

to the straight chains of the dye molecules. The non-substantivity of disazo dyes from benzidine substituted in the *o*-position to the diphenyl linkage has been ascribed to alteration in the co-planar arrangement of the diphenyl rings, any deviation from a straight linear structure leading to diminished substantivity. The hypothesis has its limitations and exceptions, but it might offer useful clues to the relation between the substantivity of a detergent and the presence in the molecule of straight chains of carbon atoms which may lie adsorbed on the glucosidic chains of cellulose. (2) The effect of the acid amide group ($-\text{CO}-\text{NH}-$), as evidenced for instance by the much greater substantivity of Naphtol AS in comparison with β -naphthol, is well recognised. The admitted efficiency of a condensation product of oleic acid and taurine as an auxiliary in the scouring of cotton may be cited in this connection; the wetting and detergent properties of a series of compounds derived from fatty acids and aromatic amines, and possessing, therefore, the common feature of an acid amide group, have proved to be of practical interest.^{5,13,14} Textile assistants are produced by condensing a sulphonic acid of phthalic anhydride with an amine containing a higher alkyl group, e.g., methylhexadecylamine or *p*-aminostearanilide, the latter compound carrying two acid amide groups (*Brit. Pat.* 461,054). Perhaps the commonest method in the patent literature of bridging a long and a short aliphatic chain is by means of an acid amide group; e.g., amino-acids (glycine, alanine, etc.) are acylated with high molecular fatty acids (*U.S. Pat.* 2,063,987; *D.R. Pat.* 635,522). Schirm's suggestion that enolisation of the acid amide group to $-\text{C}(\text{OH})-\text{N}-$ is responsible for the substantivity of Naphtol AS and his deduction therefrom that substantivity is due to the existence in a dyestuff molecule of a chain of conjugated double bonds must be subjected to more careful scrutiny. Assuming for the moment that substantivity plays a part in detergency, it should be noted that acyl derivatives of secondary amines appear in general to be more efficient than the corresponding condensation products of primary amines. On the other hand, a double bond conjugated with the carbonyl is favourable to substantivity, a cinnamoylamido group in a Naphtol being more effective in this respect than a benzamido group. (3) Conflicting results have, however, been

obtained with regard to the general influence of unsaturation, as represented by a carbon-carbon double bond, on wetting and detergency. Thus the relative values of sodium laurate and oleate were frequently reversed when lauric and oleic acids were combined with various arylamine sulphonic acids. (4) Ruggli regards the sulphur atom as being favourable to substantivity; restricted to definite groupings containing sulphur, evidence may be advanced in favour of the suggestion. Primuline containing a thiazole ring is a well-known example of a substantive dye. The high affinity of sulphur dyes in sodium sulphide solution is probably associated with the formation of $-\text{SNa}$ groups. So far as detergents are concerned, sulphonic, sulphuric and thiosulphuric groups are common features, though the evidence of their effect on wetting and detergency is not conclusive. Their influence in increasing solubility in water is obvious, but the introduction of acid sulphate and sulphonic groups does not necessarily improve wetting or detergent power; the opposite effect may frequently be encountered on account of the balance of the detergent being upset by the disproportionate influence of the ionising, hydrophilic part of the molecule. Wetting and emulsifying agents containing a sulphide linkage have been the subject of patents. One example is the sulphate of 2-hydroxyethyl cetyl sulphide (*U.S. Pat.* 2,100,297). Saponaceous organic sulphides have been described by Henkel and Co. (*Brit. Pat.* 470,717). Compounds having the formula $\text{R}-\text{SO}_2-\text{R}'\text{Y}$ or $\text{R}-\text{SO}-\text{R}'\text{Y}$, where R is an aliphatic radical of high molecular weight or an iso- or heterocyclic radical, R' an aliphatic radical containing fewer than 8 carbon atoms and Y a water-solubilising group, are wetting, cleansing and dispersing agents (*Fr. Pat.* 809,373; *Brit. Pat.* 461,614). (5) The influence of heterocyclic rings in increasing substantivity can be illustrated by dyes containing thiazole, pyrazolone, iminazole, pyrimidone and other ring systems. Wetting, emulsifying and detergent products prepared from heterocyclic compounds have been claimed in recent patents. The sulphonation products of higher alkyl substituted indoles (*Swiss Pat.* 191,011) and imidazole derivatives (*U.S. Pat.* 2,053,822) are two examples. (6) The fact that synthetic wetting agents and detergents are in general polar compounds assumes a special significance in its relation

to the problems of adsorption and substantivity. As pointed out by Ruggli, non-polar molecules are apparently not adsorbed. With the necessary variations for colour on the one hand and the properties of detergency, etc., on the other, a certain analogy may be drawn between substantive dyes and anion-active textile assistants. The influence of the dipole moment on adsorption and substantivity should be of as much interest in the case of wetting agents and detergents as of dyes. (7) While the multiplication of sulphonic groups increases solubility and tends to reduce wetting and detergent power, Ruggli and Braun¹⁵ noticed among a series of azo dyes that there is no relation between substantivity and water solubility. Measurements of the rate of diffusion indicated that all substantive dyes were colloidal and exhibited slow rates of diffusion, but all colloidal substances did not have an affinity for cotton. Substantivity was dependent on chemical constitution, rather than on physical factors, although the dependence of one on the other should be taken into account. The colloidal nature of the solution might in some cases lead to an apparent affinity for cotton, but absorption in such cases was reversible and of a temporary character, rinsing with cold water being sufficient to strip the fibre completely; true affinity should presuppose a definite degree of irreversibility or permanence in the attachment of the adsorbed material to the fibre. The studies of Conmar Robinson, Neale and others on the physical properties of aqueous solutions of substantive dyes have shown that substantivity is directly related to the ability of the dye molecules to form aggregates or micelles. McBain¹⁶ regarded soaps as colloidal electrolytes, i.e., as salts in which one of the ions was replaced by a heavily charged, heavily hydrated ionic micelle exhibiting a high conductivity. Chwala¹⁷ defined most textile assistants as colloidal electrolytes, the properties of which depend on the balance of their colloidal and ionic components. This factor, to the importance of which in a wetting agent reference has been made by Dean,² is a vital consideration in the synthesis of detergents. While the tilting of the scale on the fatty hydrophobic part would diminish the solubility in water, and increase the solubility in organic solvents, and *vice versa*, the special properties of the substance as a wetting agent, detergent, etc., would depend on the

nature of the two halves and on their balance. Colloidal character would appear to be much more necessary in a detergent than in a wetting agent. Hartley¹⁸ has characterised detergents as "amphipathic", indicating their unsymmetrical duality of affinity, and has demonstrated that they form micelles in solution. Micelle formation was found in some cases to run parallel to detergent action.

Classifying surface-active substances as anion-active and cation-active,¹⁹ the latter have normally no practical interest as detergents, but they have other extremely valuable properties, which have led to their increasing use as stripping agents, finishing agents for the production of permanent finishes and auxiliaries for the after-treatment of dyeings with substantive dyes. Products have been described in which both the anion and cation have active fatty components, an example being dodecylpyridinium laurate; these are devoid of detergent power.

The substantivity of textile assistants has been measured by Mecheels²⁰ at various temperatures up to 100°. The influence of pH and other factors was studied, but no attempt was made to approach the problem from the point of view of the constitution of the reagents or of wetting and detergent properties. Blow²¹ has examined the substantivity of cationic soaps (e.g., cetyl pyridinium bromide) towards wool. The adsorption rose with the pH and temperature; chlorination, followed by mild oxidation with hydrogen peroxide, accelerated adsorption and apparently modified the orientation of the cation, which was possibly attached to the wool surface by its hydrophilic head. Friedrich²² has shown that highly sulphonated oils exhibit substantivity to wool due to affinity for the basic radicals of the latter; the property was of practical importance since the more or less permanent incorporation of the fat improved the feel, softness, fullness and mechanical properties of the fibre. It should be assumed that only comparatively loose adsorption compounds are formed, as the adsorption varied with temperature, pH, etc. Chemical combination of the fibre, such as the combination of cellulose with organic ammonium halides to produce permanent finishes, cannot be included in a consideration of the substantivity of textile assistants towards fibres.

Apart from the fact that detergents are

usually emulsifying agents, Hartley²³ has demonstrated the solvent action of soaps and synthetic detergents on organic substances sparingly soluble in water. Hartley pictures such solubility as being due to the paraffin-chain ions collecting together in fairly large aggregates or micelles (of the order of 50 ions in each); when the paraffin-chain contains 16 carbon atoms (the commonest number in detergents) most of the paraffin-chain ions are contained in these micelles except at great dilutions in which the micelles break down. The grease, oil or other organic substance forms a liquid solution in the micelles. Although it may have no obvious bearing on detergency, Hartley's work on the solvent action of soap and detergents has great significance with regard to the after-treatment of azoic dyeings with soap or synthetic detergent solutions.²⁴ Experiments have been in progress in this laboratory on the type of auxiliary agent with reference to chemical constitution and properties, such as wetting, emulsification and protective colloidal action, suitable for a given azoic combination to produce the maximum fastness to rubbing. The after-treatment is usually regarded as a process of removal by emulsification of the superficially precipitated azoic pigment formed from that part of the Naphtol not substantively adsorbed and not removed by hydroextraction; a process of solubilisation must now be assumed to be at least partially responsible for the action. So far as the solubility factor in detergency is concerned, the main constitutional characteristic of a detergent is a hydrocarbon chain of a minimum length. The presence of long chain fatty residues would appear to be essential in an organic detergent, as distinct from a wetting agent; where aromatic ring systems are introduced into the molecule, this is more or less incidental and is based on the availability and cheapness of a raw material, such as a dyestuff intermediate, rather than any vital influence of the aromatic ring on the efficiency of the product as a detergent. It would be noticed in numerous patents taken out in recent years for the preparation of detergents from aromatic amines, phenols, etc., that the introduction of an alkyl group of 6 or more carbon atoms is a necessary part of the synthetic scheme; higher alkylated anilines may be rendered water soluble by the usual methods (sulphonation, condensation with

ethylene oxide and then with chloracetic acid, etc.) (cf. *Brit. Pat.* 475,867), leading to products with detergent properties. Even in the case of derivatives of the cycloparaffins, attachment of an alkyl chain is usual. *m*-Laurylamidocyclohexanyl sulphate and other derivatives of cyclohexanol containing an NH_2 , SH or a second OH group have been suggested (*Fr. Pat.* 811,478). Hydroaromatic alcohols are condensed with olefines, or alternatively alkylphenols are hydrogenated, and then sulphonated (*Brit. Pat.* 464,491).

One view regarding the importance of protective colloidal power, the third of the postulated requisites for detergent action, has been quoted.⁶ The disparity of outlook that is possible in this matter is indicated by the absence of any reference to it in a series of papers on "Wetting and Detergency".² In the practical aspects of detergency it may be taken to be an effective factor. The "Congo Rubine Numbers" of chemically pure samples of five commercial products, B (a recently introduced auxiliary agent free from natural fatty residues and from carboxyl and sulphonic groups), Y (sodium salt of oleyl *N*-methyltaurine), V (sodium lauryl sulphate), G (sodium β -olexyloxyethylsulphonate) and X (sodium diisopropyl-naphthalene sulphonate), were 0.3, 0.7, 3.2, 4.0 and 4.5 (in c.c. of 0.5% solution); the relative efficiency, decreasing in the order named, was at least in qualitative agreement with their detergent efficiency in the kier boiling of cotton and, incidentally, their utility in the after-treatment of azoic dyeings. Two of the structural features of organic compounds exhibiting this property were high molecular weight and a balance of hydrophobic and hydrophilic components. Synthetical experiments¹⁴ on fatty acid condensation products of arylamine sulphonic acids pointed to certain broad considerations in the chemical constitution of a good protective agent. Increasing molecular weight generally led to increasing protective action. Unsaturation in the fatty acid chain was a favourable factor, the oleyl derivatives being better than the saturated analogues, and the linoleyl derivatives better than the former; the apparently contrary effect of further increase in unsaturation needs to be confirmed by replacing the mixed fatty acids of linseed oil with pure linolenic acid. The free hydroxyl in ricinoleic acid exerted a favourable influence, the condensation products of ricinoleic acid with

sulphanilic, N-methylsulphanilic and naphthionic acids being the best protective agents in the series examined.

The chemical constitution of detergents may now be reduced to its essentials; a chemical classification of the closely related group of wetting agents has been attempted elsewhere.^{2,5,14} As polar compounds of more or less complex character they have a hydrophobic and a hydrophilic half. The hydrophilic or water-solubilising group or groups may be carried at convenient points in the hydrocarbon residue. The hydrophobic half is usually an aliphatic chain, but it may be aromatic, hydroaromatic or alicyclic. The aliphatic chain may be saturated or unsaturated, straight or branched. The effect of the double bond would be to reduce the hydrophobic character of the molecule and increase solubility in water. The effect of unsaturation on detergency is shown by the superiority of sodium oleyl sulphate to sodium lauryl sulphate, although the latter is the better wetting agent. It has been stated, however, that at moderate temperatures sodium lauryl, oleyl and cetyl sulphates all show about the same detergent power.²⁵ Sodium ricinoleate is a better detergent than the oleate, but if a second hydroxyl is introduced as in dihydroxystearic acid, the detergency is decreased. The orientation of the molecule at the interface would be affected by the additional hydroxyl, tending to bend the chain towards the aqueous layer and having an unfavourable influence on the ability of the hydrophobic half to penetrate into the oily film.²⁶

In the original detergents, the soaps, the hydrophilic carboxyl group was at the end of a straight chain of carbon atoms; in the simplest modification of the carboxyl, in order to obviate the sensitiveness to acids, alkaline earth salts, etc., the carboxyl was replaced by a primary alcoholic group, which was sulphonated or sulphated, the water-solubilising polar group being still at the end of the hydrocarbon chain.

Wilkes and Wickert²⁷ have divided surface-active compounds into 2 groups: in (1), of which the soaps, the fatty alcohol sulphates and the Igepons are examples, the polar group is a primary one, located at the end of the non-polar portion of the molecule; in (2), of which the Tergitols²⁷ (secondary alkyl sulphates), the Aerosols (esters of sulphosuccinic acid) and the Nekals are examples, the polar group is in a secondary

position, the hydrophobic chain extending from it in two directions. The inclusion of the Igepons in (1) is of doubtful advantage, since the water-solubilising group is not present at the end of an unbroken chain of carbon atoms, but of one interrupted by a hydrophilic group. Wilkes and Wickert found that products of the first group were better detergents, but were inferior to the second group with regard to wetting power. While the first part of the conclusion is justified, it has not been possible to confirm the latter in its entirety. Examined by the interfacial tension or Herbig number methods, the secondary alkyl sulphates were not better wetting agents than the primary alkyl sulphates and Igepon T; but under prescribed conditions a recently marketed substance, having the structure of a dioctyl ester of sulphosuccinic acid, was found to give the highest Herbig number among the available wetting agents. The superior detergent power of compounds carrying the polar group at the end of the straight non-polar chain might be related to the facile adsorption of the linear chains on the cellulose macro-molecule, i.e., to some factor of substantivity. At the same time, as a result of the varied and sometimes mutually opposed considerations involved in wetting and detergency, lengthening of the linear chain in order to obtain a certain favourable physical character of the aqueous solution might lead to lowering of the surface activity of the reagent on account of the tendency of the hydrocarbon residues to associate.²⁸ Branched chain derivatives might, therefore, have their points, as witnessed by the many patents covering possibilities in this direction. The secondary alkyl sulphates have been mentioned.

The acid sulphate ester obtained by the low temperature sulphation of 2-butyl-1-octanol has been claimed to be a good detergent (U.S. Pat. 2,077,005). Branched chain olefines containing at least 8 carbon atoms and one double linkage at the end of the chain are sulphonated (U.S. Pat. 2,061,617). Sulphation of tertiary alcohols, prepared by the interaction of vegetable oils with Grignard compounds, has been covered (U.S. Pat. 2,084,253). Triphenylmethane derivatives (e.g., the condensation product of 2 mols. of 2-chloro-4-amyphenol with 1 mol. of benzaldehyde-2-sulphonic acid) have high capillary activity in acid, neutral and alkaline solutions (Fr. Pat. 816,959).

The hydrocarbon chain may be interrupted or bridged by hydrophilic groups, leading to a better balanced detergent molecule. Unsaturation, signifying unshared electrons, is hydrophilic in character. The usual hydrophilic centres in a wetting agent or detergent are derived from atoms and groups exhibiting co-ordinate covalency—nitrogen, phosphorus, sulphur, oxygen, and their combinations. Examples of subsidiary hydrophilic elements and groups utilised for bridging two hydrocarbon residues (one of which may be aromatic or alicyclic) are -O-, -S-, -SO-, -SO₂-, -CO-, -CO-O-, -NH-, and -CO-NH-, the last, for reasons of its influence in favouring adsorption of the molecule by cellulose, being the commonest. Thus, sulphonated mixed ketones, R-CO-R', in which R is an aryl or heterocyclic radical and R' is an alkyl radical containing at least 6 carbon atoms, are detergents resistant to hard water (U.S. Pat. 2,089,154). Mixtures of aliphatic ketones and aromatic hydrocarbons are sulphonated to yield detergents (U.S. Pat. 2,081,795). Many of the synthetic possibilities in this regard have been covered by a wide patent of the I. G. (Brit. Pat. 479,835; 479,897) in which the products have the general formula (A)_n X.B.C-, where (A)_n stands for alkyl groups substituting X, an aromatic or cycloaliphatic group, B is an interrupting group (O, NH, S, etc.), and C a short alkyl chain.²⁸

The most frequently employed ionogenic hydrophilic part of detergents is the sulphonie or sulphuric group. The earlier view of the undesirable nature of the carboxyl group has undergone a change²⁹ and among the commercial wetting agents and detergents are several containing both carboxyl and sulphonie or sulphate groups. Modification of the carboxyl by esterification or amidation using alkyl or arylamines results in a lengthening of the chain, which may be one reason for the improved wetting and detergent properties. Next in importance to sulphonate and sulphate groups as water-solubilising groups are thiosulphate, phosphate, pyrophosphate and borate groups, which are still more or less restricted to the patent literature.

Modification of the carboxyl and solubilisation of the fatty acid derivative without the introduction of strongly ionising groups, such as sulphonie and sulphuric, may be effected by the multiplication of hydroxyls; thus the partial esterification of pentaglyce-

rol with coconut oil fatty acids yields a good detergent resistant to hard water (Brit. Pat. 439,435; 442,950).

Reference has been made to the recently marketed Igepals, which have excellent stability and detergent properties, and which contain no carboxyl, sulphonie or other ionogenic groups. They are soluble in water by virtue of other modifications in the aliphatic residues, and are highly polymerised compounds synthesised by systematic building up from low molecular units.

- ¹ Cass, *Amer. Perfumer*, 1935, **30**, 243, 260.
- ² *Wetting and Detergency*, A. Harvey, London, 1937.
- ³ Adam, *J. Soc. Dyers Col.*, 1937, **53**, 121; Conmar Robinson, *Wetting and Detergency*, 1937, p. 137.
- ⁴ Forster, Uppal and Venkataraman, *J. Soc. Dyers Col.*, 1938, **54**, 465.
- ⁵ Dhingra, Uppal and Venkataraman, *ibid.*, 1937, **53**, 91.
- ⁶ Zakarias, *Alexander's Colloid Chemistry*, New York, 1932, **4**, 654.
- ⁷ Crowe, *Amer. Dyes. Rep.*, 1938, **27**, 94.
- ⁸ Evans, *J. Soc. Dyers Col.*, 1936, **52**, 44.
- ⁹ Rhodes and Brainard, *Ind. Eng. Chem.*, 1929, **21**, 60.
- ¹⁰ Gotte, *Kolloid. Z.*, 1933, **64**, 222, 327, 331.
- ¹¹ Ramachandran, Uppal and Venkataraman, *J. Soc. Dyers Col.*, 1938, **54**, 520.
- ¹² Ruggli, *ibid.*, Jubilee Issue, 1934, p. 77.
- ¹³ *Brit. Pat.*, 343,524; 343,872; 343,899; 343,906; 452,139; *Fr. Pat.*, 797,631; 816,667; *Ind. Pat.*, 22,216; 24,057.
- ¹⁴ Uppal and Venkataraman, *J. Soc. Dyers Col.*, 1939, **55**, 125.
- ¹⁵ Ruggli and Braun, *Helv. Chim. Acta*, 1933, **16**, 858, 873.
- ¹⁶ McBain, *Alexander's Colloid Chemistry*, New York, 1932, **1**, 137-64.
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