

SYNTHETIC WETTING AGENTS
AND
COMPUTERISED
DERIVATIVES OF CASHEW NUT SHELL OIL

A Thesis

submitted by

B. D. TILAK, B.Sc.(Tech.)

To

The University of Bombay

For the Degree of

Ph.D.(Tech.).



KV
661.185.7(043)
TIL

Contents

	Page
<u>INTRODUCTION</u>	
Uses of synthetic wetting agents	1
Selection and testing of wetting agents	6
Development of synthetic wetting agents	14
Structural features of synthetic wetting agents	18
Present work	25
Preparation of oarboxylamides in aqueous solution	40
Measurement of interfacial tension <i>Continue</i>	44
Dispersibility of calcium soaps of saturated fatty acids <i>Continue</i>	46
Use of sulphamic acid as a sulphonating agent	49 <i>Continue</i>
Derivatives of cashew nut shell oil	52
Chemistry of cashew nut shell oil and its derivatives	54
Wetting agents and antiseptics from cashew nut shell oil	56
<u>EXPERIMENTAL</u>	
Preparation of C-alkoxyaniline and C-alkylaniline sulphonic acids	64
Synthesis of new wetting agents:	
(A) Derivatives of lauric acid	75
(B) " oleic acid	78
(C) " coconut oil fatty acids	79
(D) " o-toluidine-2-suluhonic acid - and fatty acid chlorides	81

	<u>Page</u>
Properties of the new synthetic wetting agents:	
Qualitative stability tests	83
Determination of wetting power:	
(a) Herbig number	64
(b) Time of sinking	96
(c) Determination of calcium soap dispersion power	101
(d) Congo Rubine number	108
Aqueous method for preparing oarboxylamides	111
Determination of interfacial tension	117
Dispersibility of calcium soaps of saturated fatty acids	121
Preparation of pure lauric acid	124
Sulphonation of aniline by sulphamic acid	127
Derivatives of cashew nut shell oil	130
Properties of the wetting agents prepared from cashew nut shell oil:	
Qualitative stability tests	148
Determination of wetting power:	
(a) Herbig number	149
(b) Time of sinking	149
(c) Determination of calcium soap dispersing power	150
(d) Congo Rubine number	152
Determination of antiseptic power	153
Summary	157
List of compounds	162

Introduction.

Uses of synthetic wetting agents:

In the past few years the old auxiliaries, such as the oils, fats, waxes and soaps which the finishers used to such good advantage have been supplemented by synthetic chemicals from organic laboratories. It would seem that organic chemistry has been pressed into service to discover new compounds, so that the textile processor may the better and more easily modify yarns and fabrics in those directions where the natural fibres are lacking (Hunter-Turner, Amer. Dyestuff Rep., 1941, 30, 371). These products possessing diversified properties of interest in textile processing have been described by the generic name "textile auxiliary agents" and are used in every stage of the conversion of raw cotton, grey yarn or cloth to finished fabric. These substances are surface active compounds of more or less complex character, belonging to the aliphatic, aromatic, hydroaromatic and heterocyclic series, and possessing one or more properties of wetting, emulsification, detergency, dispersion of calcium soaps, promotion of level dyeing, softening of textiles, and the ability to impart a special feel or handle to the fabric. Surface active agents appear in literature as wetting agents, cleaning agents, levelling agents, dispersing agents, detergents, penetrants, emulsifying agents,

solubilisers, etc. They may be generally defined as substances which, when added to liquids, will lower the interfacial tension at the boundary of the liquid, while the term "wetting agent" is usually applied to a substance which, if added to water, will cause that liquid to give a higher degree of wetting (or to possess lower interfacial tension) against a contiguous phase than would be obtained from pure water (Bartell, Chemistry and Industry, 1941, 60, 475).

Surprise and even incredulity is sometimes expressed when it is claimed that wetting agents may be employed in such widely diversified fields as galvanizing fluxes, hair washes, textile processing, fire extinguishing fluids and cements. Tremendous advances have been made in this field which are worth consideration without relation to this or that particular product. One very significant point is that the almost universal solvent, water, possesses a comparatively high surface tension which makes difficult the wetting, spreading, and mingling of water and certain other materials. It will be obvious that any reagent which successfully reduces this inconvenient surface property must almost inevitably be capable of use in as many spheres of utility as water itself (Wakelin, Text. Col., 1939, 61, 193). Lenher (Chem. and Ind., 1941, 60, 497) has given a compendium of the uses of wetting agents, which include only those commercially established. Among these applications may be listed the following:

Textile industry:

Cotton and linen processing: The wetting of grey yarn or piece goods prior to, and during, alkali boil in the kier and subsequent chlorine bleaching and also before and during peroxide bleaching. As an addition to the dye bath on all types of machines and all kinds of colours where increased penetration and uniformity of shade are otherwise difficult to accomplish. As a dispersing agent in the dissolving of dyestuffs in order to give complete solubility and full colour value. For mixing with printer's paste to effect thorough penetration, greater colour value and increased fastness to soaping, especially when cotton goods are printed direct from the bale. As an admixture to vat colour pastes where the process calls for pigment dyeing with subsequent reduction in the fibre or fabric. For mixing with water before adding dry starch; this ensures absence of lumps, complete wetting and also solubility on boiling, to effect better penetration of the acid and greater solubility of calcium and magnesium salts in "brown souring", For treating cotton piece goods prior to shrunk finishing, to wet out grey cotton piece goods on a mangle making them instantaneously and uniformly absorbent, which is necessary prior to grey sanfaring.

Wool processing: Raw wool scouring, carbonising

assistant, dyeing with wool colours; ingredient of fulling soap to aid rinsing; felting and dyeing hat felts; in finishing to give soft feel.

Rayon processing: Penetrant agents in viscose process rayon manufacture; assistant for desulfurizing rayon; penetrant for rayon size in dyeing and finishing.

Silk and nylon processing: Assistant in soaking raw silk, in conditioning, degumming, weighting and dyeing of silk.

Processing of other fibres: Scouring and dyeing of jute, straw and hair; dispersing agent for resins in moth proofing compounds; feather washing.

Leather manufacture: ♂

Cleaning of leather prior to tanning; wetting of glazed skins for recolouring; assistant in the baking process; penetrant and levelling agent in dyeing, assistant for fat liquoring of leather.

Petroleum industry:

Penetrant in acid treatment of oil wells; assistant in flooding waters in recovery of petroleum from oil bearing sands, assistant in breaking crude oil brine emulsions.

Paper industry:

Assistant in neutral and alkaline washing of mill felts; deinking of paper stock; agent to increase absorbency of paper towels, blotting papers; assistant in beater sizing with clay and alum in calender sizing.

Metal processing:

Wetting agent for acid and alkaline cleaning with or without emulsions, especially for enamelling, assistant for wire drawing, for soldering flux in electrolyte baths, anti-pitting agent in bright nickel and copper plating.

Paint industry:

Ingredient of casein cold water paint, of lacquer emulsions, wetting agent for sanding automobile body finishes.

Cleaners and cleaning compositions:

Ingredient of radiator cleaners, shoe cleaners, dry cleaning soaps, household alkali cleaners and laundry blueing.

Agricultural uses:

Wetting agent in insecticidal and fungicidal sprays, emulsifying agent in all types of sprays.

Cosmetic industry:

Emulsifying agent in lotions and creams; ingredient of brushless shaving cream, hair lotions, of foaming bath salts and water softeners, hair dye preparations, dentrifices in liquid, pastes or powder form.

Ceramic industry:

Ingredient of cement for improving grinding and setting, foaming agent to increase bulk in manufacture of mineral wool insulating bricks, wall board.

Rubber industry:

Agent to prevent adhesion of milled rubber, in latex

compound, foaming agent in manufacture of sponge rubber articles.

Miscellaneous uses:

Wetting agent for pigments and dry cleaners; assistant for the crystal growth and formation of aggregates; for preserving green fodder; in preparation of lake colours; wetting agent for laying coal dust, and dust in air conditioning systems; to prevent fogging of safety glasses; for dry powdered foods; flotation agents, as frothers for (a) sulphite ores and (b) non-sulphite ores, phosphate rock, talc, felspar and gold.

This list is of necessity incomplete and should be taken as illustrative only of the multiplicity of uses of wetting agents. Broadly wetting agents are of potential interest in all wet processing, where wetting, penetration, emulsifying, dispersing, solubilizing and cleaning are concerned. Synthetic wetting agents today have an important place in organic chemical manufacture and in industry generally.

Selection and testing of wetting agents.

Such diverse claims are put forward for each of the different textile auxiliaries on the market that the proper selection of any particular product for the required process and its evaluation are of the utmost importance. A wetting agent, for example, may be employed at a concentration higher than the requisite amount resulting in increased cost of

working, or a product unstable to alkali may be added to the kier-boiling lye. It very frequently happens that a wetting agent may fulfil one purpose well and be useless for another. Careful assay of the product and a knowledge of the precise conditions under which it is employed with advantage in the processing operation are essential desiderata.

The primary factors influencing the selection of proper wetting agents are (1) type of wetting required, (2) rate of wetting required, (3) temperature used, (4) economical concentration, (5) hardness of water, (6) presence of other chemicals and (7) hydrogen ion concentration of agent or bath. (cf. Ackley, Rayon Text. Monthly, 1941, 22, 243-44).

Type of wetting: There appear to be two distinct types of wetting, viz., "spreading wetting" and "penetration". All known wetting agents exhibit both types of wetting to some extent, but are generally more suited for one than for the other. "Spreading" wetting depends upon lowering the interfacial tension between the surface to be wetted and water, while "penetration" wetting depends somewhat upon this and also upon other factors, which govern the rate of penetration of a porous material. The efficacy of the "spreading" wetting agent would be determined by the extent of the energy change at the interface. Hence for its evaluation adhesion tension values should be measured which necessitates the measurement of contact angles. With the apparatus devised

by Bartel (Chem. Ind., 1941, 60, 475) the contact angles could be measured accurately and the results could be easily reproduced and duplicated. The "spreading" wetting power has also been determined in terms of surface tension and spreading coefficients (Cupples, Ind. Eng. Chem., 1935, 27, 1219; 1936, 28, 60, 434), of the interfacial tension between the wetting agent solution and an oil (usually as the drop number determined by means of a Donnan pipette or a stalagnometer, Romain and Knapp, Amer. Dyestuff Rep., 1936, 25, 341; Snell, Ind. Eng. Chem., 1932, 24, 1051), and of other factors such as the emulsification of greasy material from metal surfaces (the degree of cleaning being measured photographically, Morgan and Lankler, Ind. Eng. Chem., 1942, 34, 1158). Among the many fields in which surface wetting plays an important part may be mentioned the manufacture of paints, varnishes, sprays, insecticides and commercial emulsions (Clayton, "Theory of Emulsions", 1935). It is also an important factor in many problems of bacteriology and biochemistry. The improved "pendant drop" method (static) is used in measuring surface tensions by Andreas and Tucker (Ind. Eng. Chem., 1939, 31, 32). In "penetration" wetting in addition to the lowering of interfacial tension certain penetration is also effected. The comparative efficiencies of wetting agents of the "penetrating" type are governed by the relative quantities of their aqueous

dispersions which are absorbed by a constant weight of material in a given time at a definite temperature. The textile processor is more concerned with the latter aspect of wetting which is evaluated by the Draves test or the flotation test which is considered the best for laboratory evaluation of wetting agents (Draves and Clarkson, Amer. Dyestuff Rep., 1931, 20, 201; 1939, 28, P425). It can also be ascertained by determining the moisture retained by the fabric which is a direct indication of the success with which it may be submitted to the processes of desizing, scouring, bleaching, dyeing, mercerisation and finishing (Herbig, Die ole und Felte in des Textilindustrie, 1929). The modified Herbig tester (Forster, Uppal and Venkataraman, J. Soc. Dyers Col., 1938, 54, 465) provides a simple and speedy technique for determining the efficacy of a wetting agent under varied conditions of time, temperature, etc.

Rate of wetting: In many operations it is desirable to wet fabrics instantly, as when passing them through a padding machine. In other operations, instantaneous wetting is not necessary, but thorough penetration. Some materials which prove satisfactory on the padding machine may be useless when used in economic concentrations in other operations, although most materials which are suitable in very low concentrations may also be used to advantage at a higher concentration where instantaneous wetting is desired.

In the mercerising of kier-boiled yarn or cloth, penetration of the fibres by the mercerising lye is practically instantaneous, but if the yarn or cloth is in the grey state, penetration is difficult and heterogenous. The period of 2 - 3 minutes, during which the cotton is in contact with the liquor in the machine, is not sufficient to ensure perfect and uniform action of the caustic soda on the cellulose. By adding certain wetting agents to mercerising liquors, it is possible to mercerise yarn or cloth in the grey state, i.e. without previously wetting out by a kier-boil.

Temperature used: The effect of temperature upon wetting is one of the most important factors in the selection of the proper wetting agent or penetrant. With many wetting agents the temperature of maximum efficiency is just above the cloud point. Wetting agents should be tested as far as possible at the initial and final temperatures used in a particular process.

Economical concentration: The selection of an economical wetting agent depends mainly upon the fact that various wetting agents are affected differently by dilutions. Generally speaking a small change in concentration of a fairly concentrated solution of wetting agent makes very little difference. With increasing dilution a small reduction in concentration greatly affects the wetting power until a point is reached beyond which the wetting agent is of little or no

value. For a given detergent (commercial sulphonated alcohol was tested) the detergent power increased to a maximum with concentration and then diminished at higher concentrations (Palmer, J. Soc. Chem. Ind., 1941, 60, 56-60).

Hardness of water: One of the most important properties desired in a textile auxiliary agent is its ability to resist hard water. (Dhingra, Uppal and Venkataraman, J. Soc. Dyers Col., 1937, 53, 91). In any operation involving alkali or soap or other substances containing carboxyl, sulphonic or hydroxyl groups which may form insoluble products with calcium and magnesium salts the use of hard water would lead to wastage of the reagent thus precipitated and to stains on the processed material. The insoluble calcium and magnesium soaps lead to uneven dyeing and poor rubbing fastness of direct and vat colours. Another important aspect of the ability to resist hard water is the absolute need for this property as water being a necessary solvent in the textile processing the auxiliary agent must, on the one hand not itself be sensitive to calcium, magnesium or other metallic constituents of hard water and, on the other, be capable of preventing the precipitation of such metals by the soaps, dyes or chemicals involved in the process, the salts being retained in solution or very finely dispersed colloidal suspension. A convenient method of examining the calcium soap dispersion

has been developed in this laboratory, which consists of titrating a filtered mixture of soap, auxiliary agent and calcium chloride against mineral acid (Ramachandran, Uppal and Venkataraman, J. Soc. Dyers Col., 1938, 54, 520).

Presence of other chemicals: Products used in presence of alkaline hydrosulphite, and in the application of azoic dyes in strongly alkaline baths, should be tested carefully under the conditions which obtain in practice. Moreover, the stability of the standing bath containing a wetting agent, as well as the possibility of chemical interaction between the agent and other chemicals with which it may be used should also be examined. If such decomposition does occur in some cases, it is rarely found that the products exert a deleterious action on the material which is undergoing treatment, since the percentages originally employed are invariably too low to affect ultimate results; but on the other hand, the purpose for which the wetting agent is used is defeated. The effect of added salts of different valency types on the detergent power (ability to remove olive oil from wool) of a few commercial detergents of the sulphonated alcohol type has been investigated by Palmer (J. Soc. Chem. Ind., 1941, 60, 56-60). The presence of sodium salts increased the detergent power to a maximum, which occurred at the same sodium ion concentration, viz., 0.07 - 0.1 N, for all salts and for each detergent. At higher salt concentration, the detergent power .

increased rapidly. Magnesium, calcium and barium salts also increased the detergent power, just as readily as sodium ions, but effective in much lower concentrations than sodium salts.

pH of agent or bath: It is well known that a wetting agent, which gives good results in a neutral solution, may be of little use in presence of acid or alkali. In carbonising, e.g. the wetting agent should be tested for stability with about 6 - 8⁰Tw. sulphuric acid. Agents used in dyeing of wool in presence of acid should not decompose on long boiling; here it is obvious that sulphonic acids are likely to be far more stable than sulphuric esters. The detergent power of sodium oleate is greatly increased with ~~hydrogen~~ pH. ~~ion concentration~~ It is lowered in the case of "sulphonated" alcohol with the decrease in pH, while increase has little effect. As against this, with Igepon T the detergent action falls off with increasing pH (Palmer, ibid., 1941, 60, 60-62) Creely and Compton (Amer. Dyestuff Rep., 1939, 28, P419) while testing by the Draves test, the commonly accepted test for wetting power, found that a product, which when tested with one batch of yarn was quite effective, was poor in wetting another batch of different yarn. It therefore appears that the Draves test depends to some extent on the yarn used. It was also found that each technical application of wetting

agent tends to be unique and that ordinary methods of evaluating wetting agents often do not correspond in results with actual performance in plant usage. The general conclusion may be drawn that tests of wetting agents to be used in a given process must be planned with the application in mind. The type of cloth or fibre, the ^{pH} ~~hydrogen ion concentration~~ of solution, the concentration of the wetting agent, the temperature, the methods of manipulation, all should correspond as closely as possible with actual practice.

Development of synthetic wetting agents:

The earliest known wetting agent, soap, has been used for centuries for cleansing of textiles. It is still invaluable in scouring processes, apart from its wetting out properties, though its reaction with metallic ions has always been a serious drawback. This difficulty has been overcome by the introduction of synthetic products, which have the desirable properties of the soaps, but not their defects.

As the main cause of the instability of soap to hard water was due to the free carboxyl group, synthetic products containing other solubilising groups like the sulphonic in place of carboxyl were prepared.

Turkey Red oil, which is prepared by sulphonating castor oil, is more stable to hard water than soap. By increasing

the degree of sulphonation the stability of these products to hard water was increased, and they were also not precipitated by dilute mineral acids. They are useful in the pigment padding process of vat dyeing, although as detergents they have little value.

Sulphonated and sulphated oils and soap continued to be the only wetting agents used up to the time of the first world war. In 1916 the shortage of fats in Germany had stimulated research on substitutes for natural fats, especially for industrial operations. The first synthetic wetting agents in this programme prepared from non-fatty intermediates were the alkylated naphthalene sulphonic acids and their salts e. g. isopropyl or isobutyl naphthalene sulphonic acids. These products were the first wetting agents to be used in industry outside the manufacture of textiles. These products are powerful wetting agents, but lack detergent properties. Nekal BX, Perminal W, Oranit, etc. are examples of this group.

The soaps have been redesigned by blocking the carboxyl group by esterification or amidation, while the solubilising group, the sulphuric or sulphonic group is at the end of the molecule. The Igepons are examples of this type and have been very popular for their excellent all round properties. Igepon T, which is the sodium salt of oleyl N-methyltaurine, occupies a unique position in Indian mill practice, due to its

excellent scouring and wetting property.

By the introduction of sulphuric esters of synthetic higher aliphatic alcohols, substances of the general formula $R.O.SO_3Na$, and in their properties^{equal} to the Igepons have been prepared by the complete omission of the carboxyl group. These are represented by Gardinols, Lissapol A, etc. They are not so resistant to reagents as Igepons, but are good detergents and much cheaper to produce. All the wetting agents described so far have their limitations. Soap is unstable to acids and hard water. The sulphonated esters cannot be used in strongly alkaline baths, while the sulphated alcohols are not effective in strongly acid baths. The recently marketed sulphonated aliphatic ethers, may now be used under conditions which heretofore have limited the efficiency of the other compounds. They are stable under diverse chemical conditions. They have also superior detergent and deflocculating properties. Due to their stability as against the sulphated alcohols or sulphonated esters which hydrolyse to give sulphuric acid under conditions of perspiration, they are excellent for laundry operations. Triton W - 30, Triton 720, 812, Tensol manufactured by Rohm and Haas Co., Inc., are examples of this type (Antwerpen, 1939, 31, 64, 66, and ibid., 1941, 33, 740).

The recently marketed Aerosols (OT, MA, AY) are the sulphonated esters of dicarboxylic acids. These products

indicate that the earlier view of the undesirable nature of the carbonyl group has changed in recent years (Turner, Appl. Chem. Repts., 1937, 22, 221). These products are very good wetting agents.

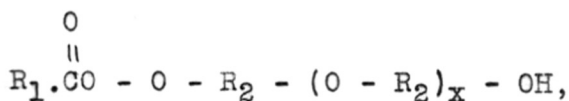
The products described so far are surface active compounds in which the non-polar group has a negative charge and are therefore anionic. Wetting agents derived from the quaternary ammonium compounds and the trivalent nitrogen amine salts in which the nitrogen is linked to at least one long chain organic radicle have been so widely used in recent years, that the surface active agents have been divided into two classes, viz., anion-active and cation active; the latter being represented by the quaternary ammonium salts. There has been a growing application of these products in the textile industry as dye auxiliaries and for finishing. A similar type of auxiliary for fixing direct dyes is to be found in certain tertiary sulphonium and quaternary phosphonium compounds which contain a high molecular weight fatty radical. These have not yet found commercial application due to their higher cost, but may be considered as pointing the way to further developments (Hunter-Turner, Amer. Dyestuff Rep., 1941, 30, 371-74; 395-98; 423-424)..

More recent and novel auxiliary agents are the Igepals, which are synthesised by polymerisation of low molecular

KN
661.185.7(043)

TIL

weight organic compounds; they do not contain ionising groups like carboxyl or sulphonic groups, but are soluble in water by virtue of other modifications in the aliphatic residues. They are good scouring and emulsifying agents (Nusslein, Melliand Textilber., 1937, 18, 248). Igepal C is mentioned as the mono-ester of an ethylene oxide polymer of the general formula



where R_1 is a hydrophobic aliphatic chain, R_2 is a short hydrocarbon residue usually C_2H_4 (Mobain and Merrill Jr. Ind. Eng. Chem., 1942, 34, 9150). Peregol O which is the condensation product of octadecyl alcohol and ethylene oxide is another example of nonionic wetting agents.

Structural features of synthetic wetting agents.

These may be summarised as follows (cf. Dean, "Wetting and Detergency", A. Hawey, London, 1937; Venkataraman, Curr. Science, 1939, 8, 281).

They are polar compounds of more or less complex character containing a hydrophobic and 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 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 oleylsulphate to sodium lauryl sulphate, although the latter is the better wetting agent. It has been stated, however, that at moderate temperatures lauryl, oleyl and cetyl sulphates all show about the same detergent power. Sodium recinoleate is a better detergent than the oleate, but if a second hydroxyl is introduced as in dihydrostearic acid, the detergency is decreased. The orientation of the molecule at the interface would be affected by the addition of hydroxyl, tending to bend the chain towards the aqueous layer and having an unfavourable influence on the stability of the hydrophobic half to penetrate into the oily film.

In the original wetting agents, the soaps, the hydrophilic carboxyl group was at the end of a straight chain of carbon atoms; to obviate the sensitiveness to acids, alkaline earth salts, etc., the carboxyl group 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.

Wilkins and Wickert have divided surface-active compounds into two groups (1) of which the soaps, the fatty

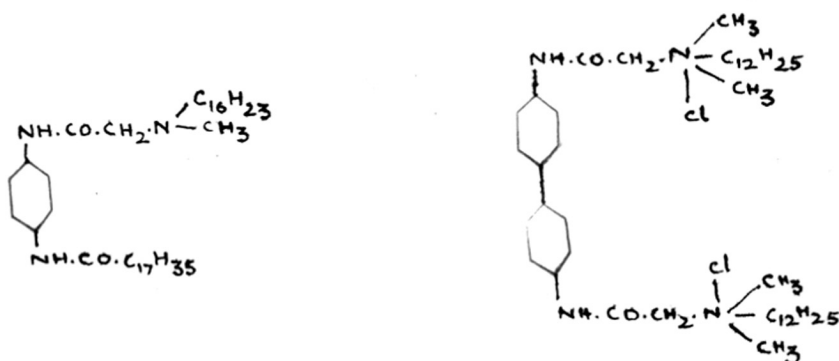
alcohol sulphates and the Igepons are examples, the polar group is a primary one located at the end of the non-polar portion of the molecule; in (2) of which the Tergitols ((secondary alkyl sulphates) the Aerosols (esters of sulphosuccinic acid) and the Nekals are examples, the polar group is in a secondary 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 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, Aerosol OT, having the structure of 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 absorption

of linear chains on the cellulose macromolecule, i.e. to some factor of substantivity at the same time, as a result of the varied and sometimes mutually opposed consideration 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. For nearly all purposes, the most effective agents are those whose hydrophilic ends exhibit a strong affinity for, or a high solubility tendency towards, the water or the hydrophilic phase and whose hydrophobic ends exhibit a strong affinity for, or a high solubility tendency towards, organic liquid or an organophilic phase. If these two tendencies are not well balanced, the efficiency of the agent may be lost through the fact that the end with the stronger character will tend to carry the molecule too completely into the phase for which the solubility is the greater (Bartell, Chem. Ind., 1941, 60, 475).

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 detergents are

derived from atoms and groups exhibiting co-ordinate co-valency nitrogen, phosphorus, sulphur, oxygen and their combinations. Examples of subsidiary hydrophylic elements and groups utilised for bridging two hydrocarbon residues (one of which may be aromatic or alicyclic) are -O-, -S-, -SO-, -SO₂-, -CO-, -C(=O)-O-, -NH- and -CO-NH-, the last for reasons of its influence in promoting the substantivity of the molecule by cellulose, being the commonest. Substantivity is one of the most important properties for a good detergent, as this allows the auxiliary to be applied from dilute solutions and yet with economy, for the liquid can be exhausted. Our knowledge of the structural features favouring substantivity of dyes is due mainly to Ruggli (J. Soc. Dyers Col., Jubilee Issue, 1934, p. 77) and the application of the same so far as synthetic wetting agents are concerned has been described by Venkataraman (Curr. Sci., 1939, 8, 283). In confirmation with Ruggli's hypothesis of symmetry as a contributory factor for substantivity we find certain novel auxiliaries developed in recent years, which are applied to direct dyes for the purpose of increasing their fastness to water and are substantive to the cellulose fibre being treated by virtue of their structural features. A large number of direct cotton dyes contain benzidine nucleus since this confers on them

substantive powers. Hence the use of this same nucleus in auxiliaries is now being considered. Other nuclei suitable for this purpose are dianisidine, 1:4-phenylene, 1:5-naphthalene diamines. In addition to these special nuclei the auxiliaries also contain long chain aliphatic radicals such as the dodecyl and stearyl radicals derived from natural fats and waxes. Two such auxiliaries are



(Hunter-Turner, Amer. Dyestuff Rep., 1941, 30, 371-74, 395-98, 423-24).

The most frequently employed ionogenic hydrophylic part of detergents is the sulphonic or sulphuric groups. The earlier view of the undesirable nature of the carboxyl group has undergone a change and among the commercial wetting agents and detergents are several containing both carboxyl

and sulphonic or sulphate groups. Modification of carboxyl by esterification or amidation using alkyl or arylamine results in a lengthening of the chain, which may be one reason for 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 sulphonic and sulphuric may be effected by the multiplication of hydroxyls; thus the partial esterification of pentaglycerol with coconut oil fatty acids yields a good detergent resistant to hard water (B.P. 439,435; 442,950).

Reference has been made to the recently marketed Igepals, which have excellent stability and detergent property and which contain no carboxyl, sulphonic or other ionogenic groups. They are soluble in water by other modifications in the aliphatic residues, and are highly polymerised compounds synthesised by systematic building up from low molecular units. Igepal C is mentioned as an ethylene oxide polymer and Paregol O as the condensation product of octadecyl alcohol and ethylene oxide (McBain and Merrill Jr. loc. cit.). The newly developed cation-active wetting

agents are capable of combining with the cellulose or protein fibre to which they are applied by virtue of their distinctive electrochemical properties and thus produce modifications of the properties of the textile material which are quite permanent in character.

Present work:

The present work represents further synthetical experiments in the programme of study on the relation between chemical constitution and properties of textile auxiliaries carried out in this laboratory. The basis of the present investigation is the undoubted efficiency of Igepon T, the sodium salt of oleyl-N-methyltaurine, as an auxiliary in the processing of cotton. Among the numerous commercial textile auxiliary agents available, Igepon T finds general favour in the Indian textile industry, due probably to its excellent all round properties, although examples of products which are superior to Igepon T with regard to a specific property may be cited. One of the structural features of this product is the presence of an acid amide group, which has been described by Ruggli (loc. cit.) Ruggli and Braun, Helv. Chim. Acta, 1933, 16, 858, et sequa), together with other constitutional features in organic compounds, as being associated with substantivity. The possession of a certain amount of affinity towards a textile material is likely to increase the

efficiency of a product as a wetting agent. On the other hand the difficulty in final rinsing off in laundrying and continuous operations of a scouring agent which is highly absorbed by textiles must be considered (Antwerpen, Ind. Eng. Chem., 1939, 31, 64).

The presence of the acid amido group might be regarded mainly as a means of linking a fatty acid chain and taurine. The very frequent occurrence in patent literature of wetting agents containing an acid amido group has been mentioned in a recent paper from this laboratory (Shirolkar and Venkataraman, J. Soc. Dyers Col., 1941, 57, 41). The condensation of fatty acids with aromatic amines and their sulphonic acids, followed by sulphonation in the former case to give synthetic wetting agents, has been the subject of several patents by Bohme,, I. G. Farbenindustrie, and the Imperial Chemical Industries (B.P. 343,524; 343,872; 343,899; 343,906). These and other synthetic wetting agents described in literature were only subject to qualitative tests and no co-ordinated and comprehensive study of the relation between the chemical constitution and their properties as textile auxiliary agents is reported.

The general conclusions regarding the relation between chemical constitution and the properties of the compounds described in the earlier work (Uppal, and Venkataraman,

J. Soc. Dyers Col., 1939, 55, 125) were that the ricinoleic acid derivatives were superior to the oleyl analogues with regard to wetting power (Herbig number), but inferior with regard to resistance to hard water, and to wetting power in terms of drop number. The influence of an N-methyl group in sulphanilic acid had a favourable influence on both the wetting power and resistance to hard water. The naphthionic acid derivative from oleic acid had lower wetting power than the sulphanilic acid derivatives. Oleic acid and ricinoleic acid were then replaced by a series of saturated fatty acids, from caproic to stearic acid, in the condensation with sulphanilic acid to study the effect of the length of the alkyl chain, and it was found that solubility in water decreased steadily with increase in the number of carbon atoms, but the Herbig number which rose continuously up to C₁₂, i.e. the lauric acid derivative, became practically constant when the alkyl chain was further increased. The calcium soap dispersing power increased up to the capric acid derivative (C₁₀) and then began to fall. By increasing the unsaturation in the fatty acid part, as in linoleic acid derivative of sulphanilic acid, the wetting power was found to decrease while the solubility increased.

In order to determine the influence of the position of the sulphonie group with respect to the amino group, sulphanilic

acid was replaced by metanilic and orthanilic acids in the condensation with oleic acid, and corresponding compounds from naphthenic acids were also prepared. In the case of the oleic acid derivatives, it was found that the o-compound was superior as a wetting agent to the p-compound, which in turn was better than the m-compound. The solubility decreased with the change from o- to m- and m- to p. The protective action and calcium soap dispersing power of the m-compound proved to be more and of the o- less than those of the p- compound. The m- and p-compounds possessed higher interfacial tension, as indicated by drop number than the o-compound. In the naphthenic acid derivatives the m-compound, the oleyl analogue of which gave a lower Herbig number than the p- or o-isomerides, gave a much higher value, but the time of sinking remained lower for the o-compound, which also proved to be a better protective agent than its two isomerides.

In the second part of the work (Shirolkar, M.Sc.Tech. Thesis, Univ. of Bombay, 1939; J. Soc. Dyers Col., 1941, 57, 41) a further series of synthetic wetting agents -
- are described. In order to study the effect of the length of the N-alkyl chain in oleyl-N-alkylanilide-p-sodium sulphonate, a series of compounds were prepared by condensing oleyl chloride with N-methyl-, N-ethyl-, N-propyl-, N-butyl- and isoamylaniline-p-sulphonic acids. It was found that with the

increase in the length of the alkyl chain, the solubility, the wetting power (Herbig number), the calcium soap dispersing power, as well as protective colloidal action, decreased, while the interfacial tension was lowered, showing that in general while N-methyl group was a favourable factor there is no advantage in increasing the size of the alkyl group. Halogenation in lauric acid compounds improved the wetting power, as tested by the Herbig number and flotation methods, while the resistance to hard water and protective colloidal action were found to be diminished. In the oleic acid compounds, no definite conclusions could be drawn. Introduction of C-alkyl group in laurylanalide-m-sodium sulphonate increased the wetting power and the protective colloidal action, but reduced the resistance to hard water as indicated by the titration method. C-Alkylation in the corresponding oleic acid analogue had a generally unfavourable influence. In the orthanilic acid compounds, while C-methylation gave a better all round wetting agent in oleic acid compounds, in lauric acid derivatives the wetting power and the resistance to hard water was reduced.

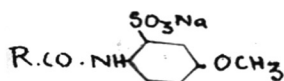
The influence of the position of the sulphonic group with respect to the amino group was studied with reference to the lauric acid derivatives of orthanilic, metanilic and ... sulphanilic acids and also with the oleic acid compounds derived from N-ethyl- and N-methylorthanilic, metanilic and

sulphanilic acids. It was found that no definite conclusions could be drawn about the influence of the relative positions of the sulphonic and amino groups on the properties of wetting agents. o-Compounds were frequently found to have the highest wetting power as examined by the time of sinking method and were also characterised by good protective colloidal action. In nearly all the cases the m-compounds were most resistant to hard water. In C-alkyl and C-halogenated anilides, m-orientation of sulphonic and amido groups gave better wetting agents (Herbig number) in lauric acid derivatives, while in oleic acid compounds the position was reversed.

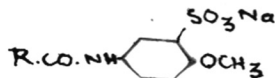
The present work is a further study of the relation between chemical constitution and the properties of newly synthesised wetting agents. In studying the properties the following determinations were made. (1) wetting power as represented by the time taken for a given weight of grey yarn to sink in an aqueous solution of the substance at 0.1 and 0.05% concentrations according to the Draves technique (Draves and Clarkson, Amer. Dyestuff Rep., 1931, 20, 201); (2) Herbig number at 5 concentrations (0.25, 0.15, 0.1, 0.075 and 0.05%) employing the modified Herbig tester (Forster, Uppal and Venkataraman, J. Soc. Dyers Col., 1938, 54, 465); (3) the calcium soap dispersing power by the acid titration (Ramachandran, Uppal and Venkataraman, J. Soc. Dyers Col.,

1938, 54, 520) and the point light methods (Hart, Amer. Dyestuff Rep., 1934, 23, 646); and (4) the protective colloidal action in terms of the Congo Rubine number (Baudouin, Melliand Textilber., 1936, 17, 654, 932; see also Ramachandran, Uppal and Venkataraman, loc. cit.).

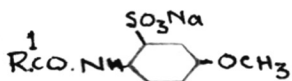
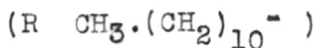
With a view to studying the influence of the O-methoxy group in the aromatic ring, *p*-anisidine-2-, and -3-sulphonic acids were condensed with lauric and oleic acids respectively yielding



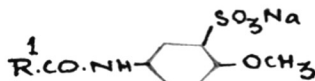
(I)



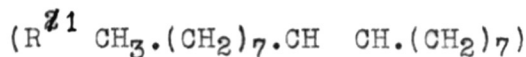
(III)



(II)



(IV)

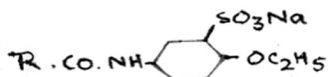


On comparing (III) with laurylanilide-*m*-sodium sulphate (Shirolkar and Venkataraman, J. Soc. Dyers Col., 1941, 57, 41) it was found that the introduction of the methoxy group improved the wetting power in terms of Herbig number

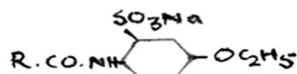
number and the resistance to hard water as tested by the titration and point light methods; while the protective colloidal action was decreased. Flotation tests, however, showed no change due to C-methoxylation. In the case of oleylanilide-m-sodium sulphonate (Uppal and Venkataraman, J. Soc. Dyers Col., 1939, 55, 125), the introduction of the C-methoxy group slightly improved the wetting power in terms of Herbig number and flotation tests, but ^{reduced} the protective action, while the resistance to hard water as tested by the point light method remained unchanged. In the lauryl derivative of orthanilic acid (Shirolkar and Venkataraman, J. Soc. Dyers Col., 1941, 57, 41), C-methoxylation made little change in the wetting and resistance to hard water as judged by the titration method, while the protective action was slightly reduced. The calcium soap dispersion, as tested by the point light method, however, was improved considerably by the C-alkoxy group.

It appeared of interest to compare these compounds with lauryl and oleyl derivatives of p-toluidine-2-, and -3-sulphonic acids to note the effect of the substitution of the C-alkoxy group in place of the C-alkyl group. The p-anisidine derivatives had ^{in general} higher wetting power judged by the Herbig number and the time of sinking and higher resistance to hard water, while the C-alkyl compounds had higher protective action. Lauryl-p-toluidide-2-sodium sulphonate was however better in all respects than the p-anisidine compounds.

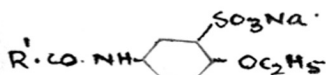
To note the effect of increase in the size of the C-alkoxy group, p-phenetidine-2-, and -3-sulphonic acids were condensed with lauric and oleic acids to yield:



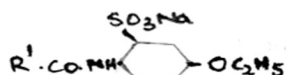
(VII)



(V)



(VIII)



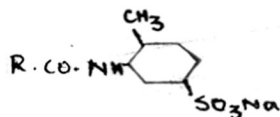
(VI)

It was found that the substitution of the ethoxyl group in place of methoxyl in (III) and (IV) was not advantageous, as the latter had better all round properties, except for protective action in the case of (IV) which was inferior to (VIII). Similar replacement in (I) and (II), however, improved the wetting power and protective action, although the resistance to hard water was reduced.

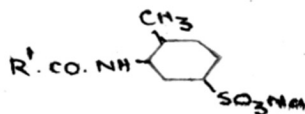
In view of the outstanding properties of lauryl-p-toluidide-2-sodium sulphonate (IX), a series of wetting agents were prepared by condensing myristic, palmitic and stearic acids and the mixed fatty acids from cocoanut, cotton seed,

groundnut and mowhra oils with p-toluidine-2-sulphonic acid, yielding compounds (X), (XI), (XII), (XIV), (XV), (XVI) and (XVII) respectively. Compound (IX), however, could not be improved upon, but the myristic and coconut oil fatty acids compounds also showed good all round properties. The mowhra oil fatty acid compound showed remarkable resistance to hard water as tested by the point light method and excellent protective colloidal action, and was better in these respects than (IX).

To study the influence of the relative positions of the C-alkyl and amino groups, lauryl and oleyl chlorides were condensed with o-toluidine-4-sulphonic acid to yield:



(XVIII)

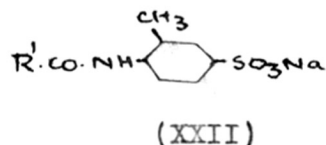
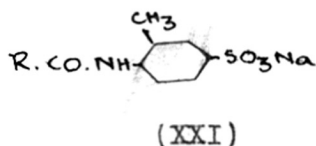


(XIX)

Compounds (XVIII) and (XIX) were then compared with the compounding p-toluidide-2-sodium sulphonates prepared earlier (loc. cit.). Lauryl-o-toluidide-4-sodium sulphonate had better all round properties than the p-toluidide-2-sodium sulphonate. The shifting of the C-alkyl group from the p- to the o-position to the amino group in the oleyl derivatives diminished the protective colloidal action, while the resistance to hard water remained the same. The wetting power

showed little change as tested by the Herbig number, although it was lower by the Draves test.

By shifting the position of the sulphonic group in (XVIII) and (XIX) from the m- to the p-position to the amino group compounds (XXI) and (XXII) were obtained.

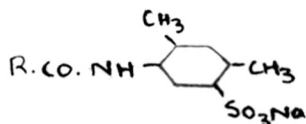


Lauryl-o-toluidide-5-sodium sulphonate (XXI) was inferior to (XVIII) in all properties. The oleyl derivative of o-toluidine-5-sulphonic acid (XXII) was less resistant to hard water than α (XIX), but both had about the same wetting power. The solubility of these compounds was less than that of (XVIII) and (XIX), in which the sulphonic acid group was m- to the amino group. On comparing compounds (XXI) and (XXII) with the lauryl and oleyl derivatives of p-toluidine-3-sulphonic acid described earlier (Shirokar and Venkataraman, loc. cit.), it was found that, in the case of the lauryl compounds, interchanging the positions of C-alkyl and sulphonic groups gave better wetting agents, but the reverse was true of the oleyl derivatives.

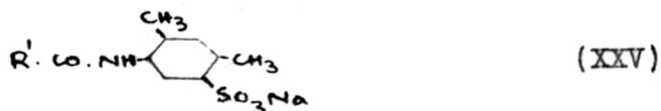
The influence of the introduction of the C-alkyl group

in the aromatic ring in lauryl and oleyl derivatives of orthanilic and metanilic acids has been described earlier. The effect of C-alkylation in lauryl and oleyl derivatives of sulphanilic acid was studied by comparing these compounds with lauryl and oleyl o-toluidide-5-sodium sulphonate (XXI and XXII). In both the cases introduction of a methyl group increased the wetting power, but decreased the resistance to hard water and protective colloidal action. The earlier observation of the favourable influence of the introduction of a C-alkyl group in sodium laurylmetanilate with respect to wetting power was confirmed by the superiority of lauryl-o-toluidide-4-sodium sulphonate, but (XIX) the new compound was also better in other properties. In sodium oleylmetanilate C-alkylation gave a better wetting agent, but the calcium soap dispersion and the protective colloidal action were decreased.

It appeared therefore that C-alkylation in general gave better wetting agents. The solubility of the substituted ~~the~~ derivatives was also higher. To observe the influence of increase in the number of the C-alkyl groups in the aromatic ring m-4-xylidine-5- and 6-sulphonic acids were condensed with lauric and oleic acid respectively, yielding



(XXIV)

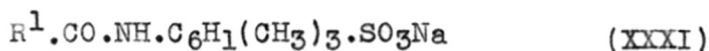
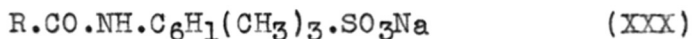


Comparing (IX) and (XXIV), it was observed that the introduction of the second C-alkyl group gave an inferior wetting agent, but increased the protective colloidal action and calcium soap dispersion tested by the point light method; the dispersion was less by the titration method. Further, C-alkylation of oleyl-p-toluidide-2-sodium sulphonate had an unfavourable influence. Compounds (XXIV) and (XXV) may also be taken as higher alkylated derivatives of lauryl and oleyl-o-toluidide-4-sodium sulphonate (Compounds XVIII and XIX). Considering the lauric acid derivatives, further alkylation decreased the wetting power, as tested by the Herbig number, but by the flotation test the di-alkylated derivative was superior; it was also more resistant to hard water as

indicated by the titration method, and a better protective colloid. Dialkylation in compound (XIX) gave an inferior product.

Dialkylation in lauryl and oleyl derivatives from p-toluidine-3-sulphonic acids gave improved the wetting power, but not the other properties.

To study the effect of further alkylation of the aromatic nucleus lauric and oleic acid derivatives of c-cumidine sulphonic acid were prepared

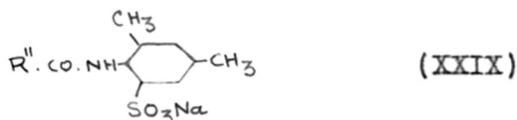


The substance (XXX) gave higher wetting power in terms of the Herbig number than the corresponding xylidine compounds at higher concentrations, but the wetting power decreased rapidly with dilution. Examined by the flotation tests it was inferior to either the monoalkyl or dialkyl substitution products. It had also less calcium soap dispersing power and protective colloidal action. As against the behaviour of laurylcumidine sodium sulphonate (XXX), the oleyl analogue (XXXI) gave a higher Herbig number in dilute solutions, while at higher concentrations the mono and dialkylated compounds were more effective. The hard water resistance was improved

and the protective colloidal action diminished by introduction of the third alkyl group in the benzene ring.

While studying the properties of the whole series of synthetic compounds, it was observed that in general the lauric acid compounds were better wetting agents as tested by both Herbig number and flotation tests, and were also more efficient with regard to the calcium soap dispersing power and protective colloidal action. The preparation of pure lauric acid from cocoanut oil is relatively expensive, and with a view to preparing wetting agents at cheaper cost the different arylamine sulphonic acids were condensed with cocoanut oil fatty acids themselves without isolation of the lauric acid derivatives. Thus *o*-toluidine-4- and 5-sulphonic acids, and *m*-4-xylylidine-5- and 6-sulphonic acids were condensed with the acid chloride from the mixed fatty acids of cocoanut oil yielding





respectively where R'' denotes the fatty acid radical. The cocoanut oil fatty acid compound from p-toluidine-2-sulphonic acid has already been described. The new compounds were comparable with the lauric acid condensates in wetting power only at higher concentrations, but were less effective in dilute solutions. Their resistance to hard water and protective colloidal action were also less than the lauric acid analogues. Where the wetting agent has to be used in concentrations above 0.25% these compounds can well replace lauric acid condensation products, although at higher dilutions the latter are much more efficient.

Preparation of carboxylamides in aqueous solution:

The wetting agents containing the carboxylamide group prepared in the present work and those described in previous communications from this laboratory were prepared by condensing the fatty acid chloride and the arylamine sulphonic acid in pyridine solution



where R = fatty acid radical; R' = aryl radical containing

the sulphonic acid group.

The action of pyridine was two-fold. It served as a solvent for the reacting substances and the resulting wetting agent and secondly as a condensing agent as it reacted with the hydrochloric acid produced in the reaction. Preparation of wetting agents on a commercial scale by this process was not possible due to the nonavailability of pyridine and its high cost. The above method was carried out under anhydrous conditions and presupposed the complete freedom of the amino-sulphonic acid from moisture and water of crystallisation. Pyridine was distilled over sodium before use. The final removal of pyridine not only resulted in the loss of the solvent, but was also a tedious operation in itself.

In B.P. 452,139 the condensation of primary and secondary alkoxyarylamine-m- or p-monosulphonic acids of the benzene series (e.g. 4-amino-1-ethoxybenzene-2-sulphonic acid) with oleyl chloride is effected in caustic soda solution below 15°C. and the resulting jelly-like paste then neutralised.

Following the same general method attempts were made to condense fatty acid chlorides with arylamine sulphonic acids in aqueous solution in the presence of alkalis. Like pyridine the alkali added served to remove the hydrochloric acid liberated in the reaction and in addition to form the sodium

salt of the sulphonic acid. Hence for each mol of acid chloride and arylamine sulphonic acid, two equivalents of alkali were added. It was found that sodium acetate could not be used in place of sodium hydroxide or carbonate. When acetone and carbon tetrachloride were used as solvents, a considerable amount of soap was formed, and the resulting wetting agent was unstable to acids and contained substantial quantities of the unreacted amino sulphonic acid. The condensation in aqueous solution when carried out at room temperature (30°C.) was unsuccessful. By carrying out the reaction at lower temperatures product containing a minimum amount of soap and free amino sulphonic acid was obtained. By mixing pure lauryl-p-toluidide-2-sodium sulphonate with different quantities of sodium laurate and p-toluidine-2-sodium sulphonate it was found that their presence, when each was less than 10% of the total mixture, gave as good wetting power and calcium soap dispersion as the pure product, allowing for the dilution. The final method arrived at gave a wetting agent in which the soap and the arylamine sodium sulphonate were below 10% and 2.5% respectively, and was taken as the optimum method. When the free soap in the final product was above 10%, the stability to hard water was reduced considerably although the wetting power remained unchanged.

Different acid chlorides like oleyl, lauryl, myristyl,

palmityl and stearyl chlorides and acid chlorides from mixed fatty acids of cocoanut, ground nut, cotton seed and mowhra oils could be successfully condensed with p-toluidine-2-sulphonic acid in aqueous alkaline solution using lower temperatures. Arylamine sulphonic acids other than p-toluidine-2-sulphonic acid were also used with success. Thus p-toluidine-5- and 6-sulphonic acids, m-4-xylylidine-6-sulphonic acid, p-anisidine-2- and 3-sulphonic acids and the corresponding phenetidine derivatives, metanilic, naphthionic, and amido-J-acids have been successfully condensed with ~~lauryl~~ lauryl and oleyl chlorides and the acid chlorides from mixed fatty acids of cocoanut oil by this method. These condensations could also be effected in pyridine solution, but the aqueous method gave a less coloured product.

The aqueous method had distinct advantages over the pyridine method in many ways. The process was cheaper as it avoided the use of pyridine, and as the cost of evaporation to obtain the wetting agent in solid form was much less, on account of the higher concentration in the reaction product. The reaction products which formed jellies or thick pastes could be marketed as such without drying or further purification. The temperature of reaction being low, a condenser was unnecessary and large scale preparation could be carried

out with simple equipment. The arylaminosulphonic acid did not need to be free from moisture or water of crystallisation. As the arylaminesulphonic acid was converted into the sodium salt before condensing with the acid chloride, the presence of free sulphuric acid in the starting material, as in the sulphonic acids obtained by sulphonation of the arylamine was not a material consideration. The products obtained by this method were lighter in colour than those obtained by the pyridine method. The wetting agents thus obtained could be conveniently adulterated with inorganic diluents like sodium chloride or Glauber's salt.

When lauryl chloride was condensed with Tobia's acid in pyridine solution, lauryl- β -naphthalide was obtained, the sulphonic group having been removed during the reaction. By condensing in aqueous solution, however, lauryl- β -naphthalide-1-sodium sulphonate was obtained.

Measurement of interfacial tension.

One of the important functions of the detergents used in scouring processes is to reduce the interfacial tension between the scouring liquor and the fabric containing oily or greasy matter, thus rendering the fabric more amenable to the action of the alkaline or other cleansing agents used. It is to be expected therefore that a good wetting agent will act as a good detergent if it can reduce this interfacial tension.

The Gardner and Holdt surface tension meter was used in the present work for determining the interfacial tension between kerosene and aqueous solutions of wetting agents.

Powney and his collaborators (Trans. Far. Soc., 1935, 31, 1510; 1937, 33, 1243; 1253; 1938, 34, 356, 363, 372, 625, 628) have studied the surface active properties of detergent solutions. Small changes in hydrogen ion concentration produced very large changes in surface tension, especially in the case of laurates and the figure obtained in presence of carbon dioxide was very different from that in its absence. The interfacial tension was also dependent on temperature. The authors have also studied the surface and interfacial tension of alkyl sodium sulphonates and xylene, using an apparatus similar to the surface tension meter used in the present ^{work}. Powney has shown that determination of interfacial tension, and hence the drop number, has little value unless the precise conditions of the experiment are mentioned. He found that curves of the interfacial tensions plotted against molar concentrations of the sodium alkyl sulphates showed well defined breaks at certain critical concentrations, which were dependent on the chain length of the alkyl group and the temperature.

In the present investigation Igepon T, Nekal BX and sodium laurate were examined as three representative types of

wetting agents, to determine the effect of increase in the concentration of the wetting agent upon the interfacial tension. Freshly distilled water was used for making the solutions and the hydrogen ion concentration values were determined. It was found that the drop number varied considerably with the rate of drops emerging from the ground end of the capillary. In a single determination, keeping the air inlet unchanged, the drops issued faster in the beginning due to the higher pressure head and then slower as the bulb was being emptied and near the end of the determination the drop rate was very slow. In determining the drop number, the "drop rate", the average time taken by 100 drops in seconds was kept as nearly the same as possible. The drop numbers were determined at 0.05 - 2.0% concentrations.

It was found that the drop numbers increased rapidly with a slight increase in concentration of dilute solutions, whereas at higher concentrations a small change in concentration led to little change in the drop number. In the case of Igepon T the increase was more gradual.

By allowing the drops to issue faster, the drop number was lowered.

Dispersibility of calcium soaps of saturated fatty acids.

The titration method for determination of hard water

resisting power of the wetting agent consisted in measuring the amount of calcium oleate dispersed by the wetting agent by titration with standard hydrochloric acid. In testing the calcium soap dispersion of soaps from saturated fatty acids the method was not satisfactory, as the soaps themselves formed calcium salts with calcium chloride. A modification for determining the solubility of calcium soaps of the saturated fatty acids and the amount of precipitated calcium soap dispersed by the dissolved calcium soap was to take equimolecular proportions of the soap and calcium chloride and the rest of the experiment followed as the titration method. An aqueous solution of the sodium soap (10 c.c. of 0.02N) was diluted with distilled water (25 c.c.) and calcium chloride solution (10 c.c. of 0.02N) was added. The precipitated calcium soap was filtered and washed as usual, and the dispersed calcium soap titrated with 0.1N hydrochloric acid, using Linstead's mixed indicator. The determination was made at room temperature (30°C.) and at 60°C. The dispersion of calcium soaps was also examined by the point light method.

The amount of calcium soaps dispersed decreased from caprylic acid to lauric acid, and then there was a slight increase, calcium myristate being more dispersed than the laurate. From C₁₄ to C₁₈ the decrease again was gradual.

In an earlier experiment the sodium soaps of palmitic, and stearic acids were in the form of jellies at 30°C. and were used as such. By using a clear warm solution in the determination, diluting with water, cooling and then carrying the test as usual it was observed that calcium soap of sodium stearate dispersed much more than when the jelly was used. By carrying out the test at 60°C. the dispersion decreased from C₁₀ to C₁₂ and then increased sharply in the case of C₁₄, and then there was a gradual increase from C₁₄ to C₁₈, calcium stearate and calcium caprylate being completely dispersed in the hot.

It was of interest to compare these results with the calcium soap dispersion of the sodium soaps saturated fatty acids described earlier (Shirolkar and Venkataraman, J. Soc. Dyers Col., 1940, 56, 503). As against the earlier observation in which sodium caprate was found to be the best dispersing agent employing 2.5 c.c. of 2% soap solution or sodium laurate when 5 c.c. of 2% soap was employed, sodium caprylate was dispersed to the maximum extent in cold and hot, and sodium laurate was least dispersed in hot. There is a remarkable difference in the dispersibility of higher saturated fatty acid calcium soaps in cold and at higher temperature calcium stearate being completely dispersed at 60°C. The higher fatty acid soaps can therefore be used even in hard water, so

long as they are used in hot, and removed from the fabric in hot. Tested by the point light method the higher fatty acid soaps were again found to be completely dispersed in hot (60°C.)

Use of sulphamic acid as a sulphonating agent.

Sulphamic acid or aminosulphonic acid, $\text{NH}_2\cdot\text{SO}_3\text{H}$ was until recently a rare substance, but it is now available commercially, and its unique properties make it a very interesting subject for study by textile chemists (Text. Col., 1942, 64, 342; Cupery and Gordon, Ind. Eng. Chem., 1942, 34, 795). Sulphamic acid is manufactured from urea and sulphuric acid (U.S.P. 2,102,350), or by passing sulphur dioxide into a saturated solution of hydroxylamine hydrochloride. It crystallises from water in rhombic form and melts at 205°C. with decomposition. It is a nonvolatile, nonhygroscopic solid, which may be handled with ease. It dissolves in water readily, giving a strongly acidic solution, and forms soluble sulphamate with metals like barium and lead.

Due to its diverse properties it has been used for a variety of purposes, some of which may be briefly stated. For determining and for removal of nitrite following diazotisation reactions in the manufacture of dyes and colour lakes and in the application of developed colours. For flame

proofing of textiles, due to the fire retarding gases evolved when it is destructively heated. Sulphamic acid salts are reported to prevent precipitation and loss in strength due to decomposition of solutions of sulphated fatty alcohols and stock soap solutions, and also to prevent deposition of lime soaps due to the solubility of calcium sulphamate. The use of sulphamic acid in the manufacture of wetting agents is mentioned in patent literature (B.P. 382,942 and 455,893; U.S.P. 2,212,171). It is also widely used in tanning and in agriculture as ammonium sulphamate which has outstanding herbicidal action (Cupery and Gordon, loc. cit.). Among other miscellaneous uses may be mentioned its use as a laundry sour, fixing agent for dyes and as a textile finishing agent.

In the present work the use of sulphamic acid as a sulphonating agent has been studied. It was used by Salzberg (U.S.P. 2,212,171) for solubilising amines containing C₈-C₁₈ in a straight chain to form compounds of the general formula

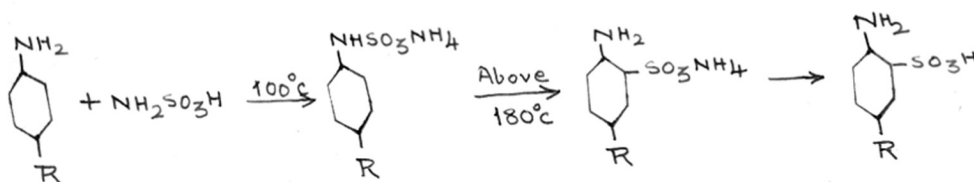


where R is alkyl of C₈-C₁₈, and R¹ and R² may be H or alkyl.

Sulphamic acid was used in sulphonating arylamines. Paal (Ber., 1901, 34, 2753) sulphonated p-chloroaniline with sulphamic acid. The same general method was used in sul-

phonating p-toluidine by Shirolkar (loc. cit.). In either of these cases arylamine sulphonic acids in which the sulphonic group was o- to the amino group were obtained.

In the present work, sulphamic acid was employed for sulphonating p-anisidine and p-phenelidine, the sulphonic acid group being introduced o- to the amino group. The probable chemical action taking place during the reaction may be represented as follows (Paal, loc. cit.)



where R represents a substituent like halogen or alkyl.

In each of the arylamines sulphonated, the p-position to the amino group was occupied by a substituent. Hence It was concluded that sulphamic acid offers a convenient method of preparing amino sulphonic acids in which the amino group is o- to the sulphonic group.

To study the orientation of the sulphonic group in unsubstituted arylamines, aniline was treated with sulphamic acid. The sulphonic acid crystallised in hexagonal plates and was characterised by preparing the p-toluenesulphonyl derivative, m.p. 265° , which was identical with the derivative from

·sulphanilic acid described previously by Uppal and Venkataraman. On treating the substance with p-chloraniline hydrochloride; the arylamine salt was obtained (melting point $236^{\circ}\text{C}.$) and was identical with the p-chloraniline salt of p-tolunesulphonyl sulphanilic acid. It was therefore concluded that in sulphonating with sulphamic acid the sulphonic group was directed normally p- to the amino group, but to the o- position if the position was already occupied by substituents as in the case of p-chloroaniline, p-anisidine, or p-toluidine.

Derivatives of cashew nut shell oil.

The cashew nut is a fruit of an ever green tree, Anacardium occidentale Linn belonging to the natural order Anacardiacea. The tree is indigenous to South and Central America and India. The outer covering of the cashew nut contains a reddish brown oil, the removal of which is difficult due to its corrosive nature. The usual method used is to roast the nuts, when the oil cells of the shell burst and the oil oozes out. In India, raw cashew nuts were roasted only for the kernel until recently, the shells being regarded as a waste product. The oil, however, can be used to advantage as a raw material for preparing synthetic products due to its availability and cheapness. The oil/also^{can}

be obtained from the shells by extracting with solvents.

Cashew nut shell oil was first used by Harvey as a raw material for the manufacture of varnishes and impregnating materials known as "Harvel", "Oil stop" and "Cardolite", and since then it has been used extensively for a variety of purposes. The application of the oil is based on its property of polymerising when heated at 100-200°C. with an acid or alkaline catalyst, and of forming condensation products with aldehydes, apparently because of its phenolic constituents. Some of the applications of the oil may be listed as follows

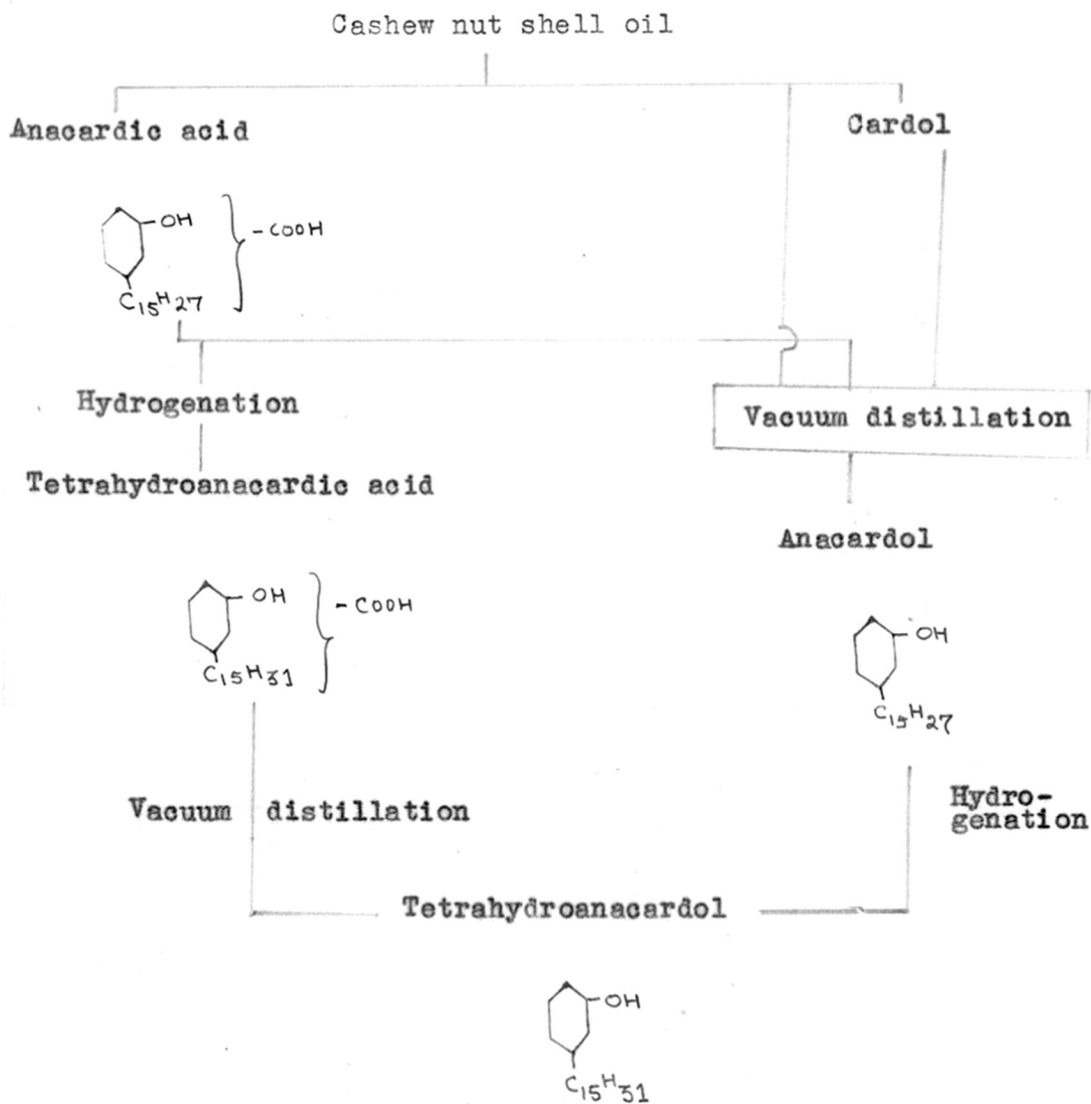
Harwelwood pitch and heat-treated cashew fluid form a petroleum insoluble composition that can be used for coating or impregnating (Harvey, U.S.P. 1,725,724; 1,725,795). A substitute for shellac is obtained by heating the oil to 140-200°C. with copper aluminium or lead or their derivatives. After removing the metallic constituents, a liquid product is obtained which is used as a varnish (Harvey, U.S.P. 1,725,793), and for coating and impregnating. It is used in water-proofing compositions for walls (Harvey, U.S.P. 1,977,826); in artificial rubber compositions, ~~with sulfur, xresins~~ ~~with sulfur, xresins~~ and as a plasticiser for cellulose products (Harvey, U.S.P. 1,838,071). By distilling the oil (B.P. 305-400°C) a germicide is obtained. Cardanol-formaldehyde resins are soluble in drying oils and are therefore widely used.

Chemistry of the cashew nut shell oil and its derivatives.

Stadeler (Das Annalen der chemie und der Pharmacie, 1884, 63, 137) showed that the extracted oil contained two components, one acid, which he called "Anacardic acid", constituting 90% of the oil and the remaining 10% called "cardol". Ruheman and Skinner (J. Chem. Soc., 1887, 51, 663; and Sudborough, J. Ind. Inst. Sci., 1923, 15, 133) gave the molecular formula of anacardic acid as $C_{22}H_{32}O_3$ and showed that it was a hydroxycarboxylic acid. Smit (Proc. Acad. Sci. Amsterdam, 1931, 34, 165) isolated anacardic acid and showed it to be a homologue of salicylic acid, having an unsaturated alkyl chain $C_{15}H_{27}$, attached to the nucleus. Spiegel and co-workers (Ber. deut. pharm. Ges., 1895, 5, 309; 1913, 23, 356) studied stadeler's "cardol" and gave it the formula $C_{32}H_{30}O_3.H_2O$, and considered it to be a phenol. The position of the hydroxyl group has been proved to be m- to the alkyl group by Patel and Shah (Curr. Sci., 1940, 9, 363). The position of the carboxyl group has not yet been determined, but in all probability it appears to be sandwiched between the ~~alk~~ alkyl and the hydroxy group, in view of the difficulty in direct esterification.

By vacuum distilling anacardic acid, decarboxylation takes place and anacardol is obtained. It can also be prepared by vacuum distillation of the shell oil, either

extracted or commercial, and of the "cardol" residues left after removal of anacardic acid (Gandhi and Venkataraman, J. Ind. Chem. Soc., Indl. Ed., 1942, 5, 93). Anacardic acid and anacardol on hydrogenating give tetrahydroanacardic acid and tetrahydroanacardol. The chemistry of the derivatives of the shell oil may be summarised as follows



Wetting agents and antiseptics from cashew nut shell oil.

One of the serious problems in the textile industry has been the danger of mildew attack. Mildew organisms under favourable conditions grow profusely on the fabric, causing damage and rendering it unsalable. To overcome or to inhibit mildew growth, various antiseptics have been recommended. Zinc chloride is one of the oldest in use, but due to its defects other and more expensive substances, such as phenols, cresols, phenolic acids and their derivatives have come increasingly into vogue, to which the generic name "Textile antiseptics" is given. Greshenfeld and collaborators have studied the antibacterial aspects of wetting agents, and their influence upon the efficacy of antiseptic materials (Amer. J. Pharm., 1941, 113, 306). Antibacterial action is conditioned by a favourable combination of the following three factors (1) the existence of a surface active group, anionic or cationic, (2) the hydrogen-ion concentration of the environment and (3) the susceptibility of the micro-organism. Anionic compounds like Aerosol OT, Tergitol 4 and 4T and cationic compounds like "Tritons", were studied. The latter showed greater efficiency in alkaline range and were more active against Gram-negative *Eberthella typhi* than against Gram-positive *staphylococcus aureus*. As against this, the anionic type like Aerosol OT exhibited the reverse behaviour. When Aerosol OT in a nonbactericidal concentra-

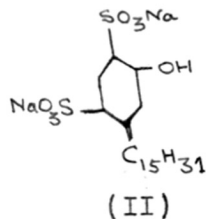
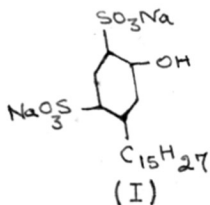
tion was combined with different antiseptics, like phenol, mercuric chloride and "Zeonite", their efficacy was increased with increase in hydrogen ion concentration. On the other hand a number of wetting agents when added in concentrations of 0.1 to 1% to phenol composition did not increase their bacterial action. Ozdal, Wilson and Borg (J. Bact., 1941, 42, 117) concluded from their experiments on the additions of wetting agents to buffered solutions of phenolic compounds, at various degrees of alkalinity (from pH 9 to pH 11) that the effective wetting agents intensified the antibacterial action of the undissociated phenols rather than the phenolates. The wetting agents used were sodium laurate and oleate and sodium lauryl sulphate.

Anacardic acid, which forms the main constituent of cashew nut shell oil, has wetting and detergent properties as anticipated from its constitution as a C-pentadecadienyl-salicylic acid; the Herbig number of a 0.5% solution of sodium anacardate is 62.2, which compares favourably with the figures for the wetting agents commonly used in the textile industry. Substantivity experiments on mercerised cotton indicate that both sodium anacardate and tetrahydroanacardate are preferentially absorbed from aqueous solutions. Its practical utility in textile processing is, however, limited due to its instability to hard water, heat and oxidising agents.

In view of its known antiseptic action derived from its phenolic character and the added advantage of its properties as a wetting agent for cotton, anacardic acid was used as a starting material for preparing synthetic products combining antiseptic and wetting ~~are~~ properties in the first part of the work on cashewnut shell oil derivatives commenced in this laboratory (Gandhi, Ph.D. Thesis, Univ. of Bombay, 1942; Gandhi and Venkataraman, J. Ind. Chem. Soc., Indl. Ed., 1942, 5, 75; ^{Forster,} Gandhi and Venkataraman, ibid., 85; Gandhi and Venkataraman, ibid., 89). Sodium anacardate, in addition to its high wetting power, had antiseptic value equalling zinc chloride. Various salts of anacardic and tetrahydroanacardic acids were prepared and their wetting and anti-mildew properties examined. It was found as a general rule that the wetting power and anti-mildew properties of the salts of anacardic acid were better than those of tetrahydroanacardic acid. To prepare compounds similar to salicylanilide, but which might have wetting properties in addition, anacardic and tetrahydroanacardic acids were condensed with various amines like aniline, substituted anilines, naphthylamines and benzidine, and their anti-mildew efficiency and wetting power (Herbig number) examined. They were, however, only poor wetting agents, although some of them had good antiseptic properties.

In the present work, the possibility of using cashew nut shell oil as a raw material for preparing synthetic wetting agents was further investigated, the anti-mildew efficiency being also determined. While the earlier investigation was concerned with anacardic acid, anacardol was the starting material in the synthesis of the new wetting agents, one of the chief drawbacks of anacardic acid salts being the instability to hard water.

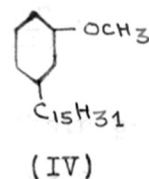
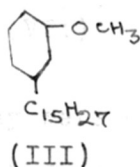
For solubilising anacardol and tetrahydroanacardol, these were sulphonated and neutralised to give anacardol disodium sulphenate (I) and tetrahydroanacardol disodium sulphenate (II)



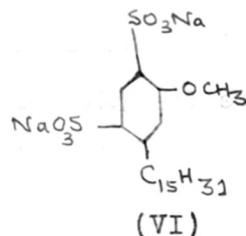
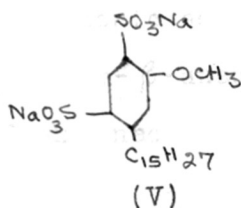
Compared with sodium anacardate and tetrahydroanacardate (loc. cit.) they had inferior wetting power, but the stability to hard water had considerably improved. The tetrahydroanacardol disodium sulphenate (II) was superior to the anacardol derivative (I) in wetting power and protective colloidal action, while the latter had more calcium soap

dispersing power.

To reduce the hydrophilic character of the compounds I and II, anacardol and tetrahydroanacardol were methylated to give o-methyl ethers of anacardol (III) and tetrahydroanacardol (IV)



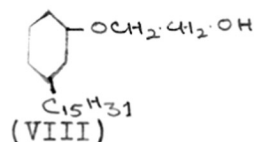
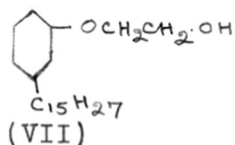
which were sulphonated to give the corresponding disodium sulphonates



respectively.

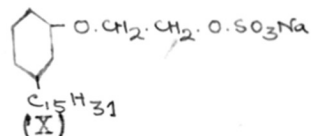
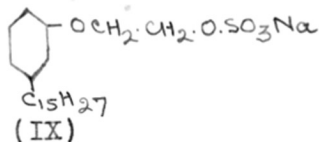
Their wetting power and protective colloidal property were better than those of the phenolic analogues, but in anacardol disodium sulphonate (I), methylation of the hydroxyl ~~decreased~~ the calcium soap dispersion, while the reverse was the case in the tetrahydroanacardol derivative. The o-methyl tetrahydroanacardol disodium sulphonate (VI) was again better than the anacardol compound (V) in every respect.

By condensing anacardol and tetrahydroanacardol with ethylene chlorophyd^rine, β -anacardoxyethyl alcohol (VII) and β -tetrahydroanacardoxy ethyl alcohol (VIII) were obtained

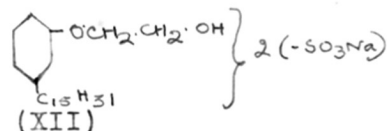
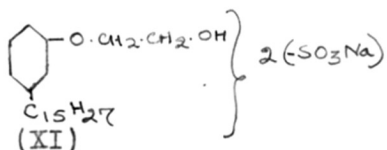


They were characterised by preparing their p-toluene-sulphonyl derivatives, α -naphthyl^{ura}methanes and 3:5-dinitrobenzoates. Similar derivatives from anacardol and tetrahydroanacardol were also prepared for comparison.

The phenoxy alcohols were then sulphated with chlorosulphonic acid, yielding on neutralisation with caustic soda sodium- β -anacardoxyethyl sulphate (IX) and sodium β -tetrahydroanacardoxyethyl sulphate (X)



Treatment with fuming sulphuric acid and neutralising gave



Both the sulphate and the disulphonate from anacardoxyethyl alcohol had greater wetting power and protective colloidal action than anacardol disodium sulphonate, but they were less resistant to hard water; the position was reversed in the case of the tetrahydroanacardol derivatives, the conversion to the ethanol derivative leading to diminished wetting power and protective colloidal action and increased hard water resistance. The tetrahydroanacardol derivatives had better all round properties than the anacardol derivatives. Most of the synthetic products described were excellent calcium soap dispersing agents; while this limitation of sodium anacardate had been removed, the wetting power had simultaneously suffered.

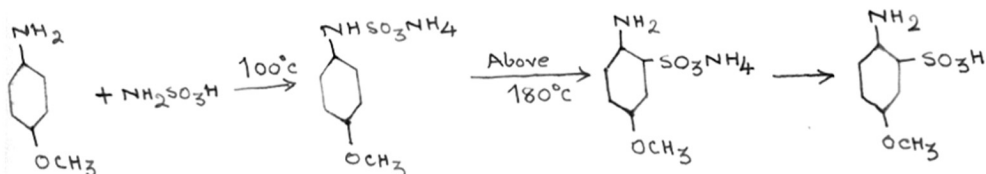
The synthetic wetting agents prepared were examined for their antiseptic properties by the cloth method described earlier (loc. cit.). The tetrahydroanacardol derivatives were better antiseptics than the anacardol compounds, and better than zinc chloride, commonly used in sizing and finishing pastes. The cashew nut shell oil derivatives were, however, poor as compared with commercial products like Shirilan,

Preventol I and Amicrol. The replacement of the phenolic hydrogen by a hydroxyethyl group (i.e. the removal of the phenolic character by etherification) did not materially alter the antiseptic value of the derivatives; the reason appeared to be that the long aliphatic chain in anacardol and tetrahydroanacardol had already diminished the phenolic function so much, as indicated for example by the sparing solubility in aqueous alkali, that conversion of the hydroxyl to a β -hydroxyethyl ether made little further difference.

Experimental

Sulphonation of p-anisidine.

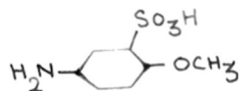
p-Anisidine-3-sulphonic acid:



The sulphonation of p-anisidine was carried out by using sulphamic acid. In analogy with the sulphonation of p-chloro-aniline by the same reagent carried out by Paal (Ber., 1901, 34, 2753) the course of the probable reaction is suggested above. p-Anisidine (30 g.) and sulphamic acid (25 g.) were finely ground together and the mixture was heated in a 250-c.c. round bottomed flask fitted with a ground glass air condenser and a calcium chloride tube. The mixture was heated to 200°C. in an oil bath and kept at this temperature for one hour. During the heating, the mixture melted and the colour changed to deep purple. In the molten condition the contents were transferred to a mortar, and after cooling the hard mass was ground and the unreacted p-anisidine, was extracted with ether. The residue was suspended in hot

water in an evaporating dish and baryta solution in excess was added. The aqueous suspension was boiled till the smell of ammonia vapours disappeared completely. To this mixture slight excess of sulphuric acid (1:1) was added and the boiling continued. The contents were then filtered and the residue further extracted thrice with 50 c.c. portions of boiling water. All the extracts were added together and cooled in refrigerator overnight. p-Anisidine-3-sulphonic acid separated as needles. These were collected and recrystallised from hot water after decolouring^z with norit. The yield was 7.5 g. The substance decomposed at 294°C. (without melting. 0.126 G. required 6.3 c.c. of N/10 caustic soda solution for neutralisation. Calc. 6.2 c.c. N-point, however, was not very sharp. The sulphonic acid gave a deep violet colour with ferric chloride and reduced ammoniacal silver nitrate on warming.

p-Anisidine-2-sulphonic acid:



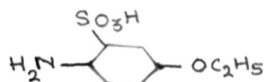
Crude p-anisidine was vacuum distilled and used for sulphonation. One part of p-anisidine (m.p. 55-56°C., 20 g.) was slowly added to 1.5 parts of 20% fuming sulphuric acid (15.8 c.c.) kept stirred in a test tube fitted with a

mechanical stirrer and externally cooled with (~~used~~ ice.

After the addition of p-anisidine the mixture was gradually brought to 100°C. in a water bath and kept at this temperature for 2 hours. Concentrated sulphuric acid (98%, 15 c.c.) was added to ensure better working of the mixture which had partially ~~sett~~ solidified. The contents were further heated at 100°C. for 2 hours when complete sulphonation took place. A test portion dissolved completely in water and the aqueous solution remained clear on adding excess of aqueous caustic soda, thereby showing complete conversion of the sulphate to the sulphonic acid. The sulphonation mixture was then poured in 200 c.c. ice-cold water (5°C.), when the sparingly soluble sulphonic acid separated as a pink coloured precipitate. It was filtered and ~~recry-~~ crystallised from boiling water (800 c.c.) after decolouring with norit charcoal. The sulphonic acid which separated as colourless needles on cooling, was collected, and dried. Yield 8 g. The product decomposed above 320°C. It gave a deep violet colour with ferric chloride and reduced Fehling solution and ~~ammoniacal~~ silver nitrate on warming (0.173 g. required 8.7 c.c. of 0.1N sodium hydroxide. Calc. 8.5. Indicator - phenolphthalein. The N-point was not sharp as the sulphonic acid oxidised to give brownish solution in the presence of alkali.

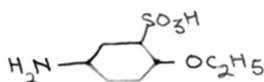
Sulphonation of p-phenetidine.

p-Phenetidene-3-sulphonic acid:



The sulphonation of p-phenetidine was carried out in the same way as p-anisidine using sulphamic acid. p-Phenetidine (2 parts, 20 g.) and powdered sulphamic acid (1.5 parts) were heated together to 200°C. and kept at this temperature for 45 minutes. As in the sulphonation of p-anisidine, the reaction mixture was deep purple. It was worked in a similar manner. The sulphonic acid was crystallised from hot water. It separates as clusters of needles (Yield 5.7 g.) decomposing above 280°C.

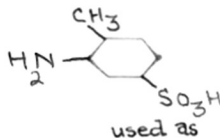
p-Phenetidine-2-sulphonic acid:



p-Phenetidine (10 g.) was slowly added to fuming sulphuric acid (20%, 11.6 c.c.) (thrice the theoretical quantity necessary) in a test tube fitted with a mechanical agitator and externally cooled with ice. The mixture was gradually brought to 100°C. in a water bath and kept ^{at} this temperature for 4 hours. The sulphonation mixture sets ^{to} a dull pink coloured solid on cooling. It was diluted with water (250 c.c.), when the sulphonic acid which being sparingly soluble separated, was

filtered, washed with ice-cold water (5°C. 50 c.c.) and finally dried over phosphorus pentoxide. The crude product weighed 15 g. It was crystallised from boiling water (2500 c.c.) after decolouring^{zi} with norit charcoal. The sulphonic acid which separated from aqueous solution as pinkish needles was collected and dried in vacuum over phosphorus pentoxide. Yield of crystallised sulphonic acid 8.5 g. The sulphonic acid decomposed above 275°C. and at 310°C. it completely carbonised. A dilute solution of the acid gave deep violet colouration with ferric chloride and reduced ammoniacal silver nitrate and Fehling solution (Titre - 0.164 g. required 7.7 c.c. of 0.1N sodium hydroxide for neutralisation. Calc. 7.6 c.c.) N-point, however, was not sharp, as the acid gave a brownish solution in the presence of alkali.

o-Toluidine-4-sulphonic acid:



o-Nitrotoluene was the starting material. It was sulphonated and subsequently reduced to give the aminosulphonic acid. ~~Nitration of o-nitrotoluene~~

Nitration of o-nitrotoluene: To o-nitrotoluene (20 g.) in a 100-c.c. 3-necked flask fitted with a stirrer, fuming sulphuric acid (10.4 c.c. 80%) was added at 0°C. under constant stirring. The temperature was gradually raised to 100°C. by h

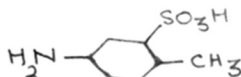
heating in a water bath and stirring continued for 4 hours when the sulphonation mixture gave a clear ~~mix~~ solution with water.

Reduction of o-nitrotoluene-4-sulphonic acid:

o-Nitrotoluene-4-sulphonic acid being extremely hygroscopic could not be isolated from the sulphonation mixture by usual methods like salting out with acetone, sodium chloride or hydrochloric acid. The sulphonation mixture was therefore neutralised and then reduced to amino compound without isolating the nitrotoluene sulphonic acid. It was poured on crushed ice (100 g.) and the residual quantity in the flask washed with little water. It was then neutralised with 50% caustic soda solution and made up to 300 c.c. The neutral solution was transferred to a 3-litre 3-necked round bottomed flask fitted with a reflux condenser and a mechanical stirrer. Concentrated pure hydrochloric acid (2.4 c.c.) was added and the contents brought to 100°C. Iron filings (23 g.) were added gradually and refluxing and stirring continued for 4 hours. The contents were then filtered hot and the residue extracted twice with 50 c.c. portions of boiling water. The filtrates were collected and concentrated to 100 c.c. and concentrated hydrochloric acid (25 c.c.) was added and the solution kept in the refrigerator overnight. Large~~r~~ amber coloured needles separated, which were purified by crystallising from water after charcoaling. Colourless needles of o-toluidine-4-sulphonic acid which separated on cooling the water extract

(14 g.) were collected and dried. The product decomposed above 280°C. (0.145 G. required 7.6 c.c. of 0.1N caustic soda for neutralisation. Calc. 7.7 c.c. N point, however, was not sharp).

p-Toluidine-2-sulphonic acid:

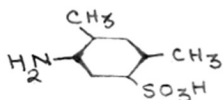


Commercial p-nitrotoluene-2-sulphonic acid was reduced by iron and hydrochloric acid to give the amine. The p-nitrotoluene-2-sulphonic acid (110 g.) was mixed with water (60 c.c.) and acidified with commercial hydrochloric acid (8.5 c.c. of 35%) in a 500 c.c. 3-necked round bottomed flask fitted with a reflux condenser and an agitator and iron filings (85 g.) were gradually added at 100-105°C., the flask being heated on a sand bath. The mixture was treated at 100-105°C. for 4 hours after further dilution with 60 c.c. of water and filtered hot. The residue was extracted twice with 50 c.c. portions of boiling water and the extracts were added together and acidified with 25 c.c. of commercial hydrochloric acid (35%) and left in the refrigerator overnight. The slight coloured prismatic crystals which separated were collected (85 g.) and recrystallised from water (70 g.) The amine decomposed above 300°C. and its aqueous solution gave a red colouration with ferric chloride and reduced

ammoniacal silver nitrate.

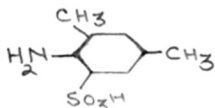
Sulphonation of m-4-xylylidine:

m-4-xylylidine-6-sulphonic acid:



m-4-Xylylidine (12.1 g., 1 mol) was added under stirring to 20% fuming sulphuric acid (15.8 c.c., 3 mols) in a 100 c.c. 3-necked round bottomed flask fitted with an agitator at 0-5°C. The mixture was gradually brought to 100°C. in a water bath and treated at this temperature for 4 hours. It set to a solid at low temperature/^{but} partially liquified on warming. Concentrated sulphuric acid (5 c.c. of 98%) was added at the end of 2 hours for better working of the mixture. After 4 hours, a test portion dissolved completely in water and remained clear on adding excess alkali, thereby signifying complete sulphonation and the absence of m-4-xylylidine-sulphate. The sulphonation mixture of ~~them~~ poured on crushed ice (50 g.) and residual quantity in the flask washed ~~down~~ with little cold water. The m-4-xylylidine-6-sulphonic acid which separated as a pinkish white solid was filtered and crystallised from 1600 c.c. of boiling water after charcoaling. The aminosulphonic acid crystallised out in the form of colourless rods on cooling. Yield 7.0 g. On concentrating the mother liquor a second crop of crystals (3.6 g.) was collected.

m-4-Xylidine-5-sulphonic acid:



m-4-Xylidine (1 mol. 15 g.) and 100% sulphuric acid (1 mol, 6.8 c.c.) were mixed in a 100-c.c. 3-necked round bottomed flask fitted with an agitator and heated in an oil bath. A current of dry carbon dioxide was swept over the mass as it was ~~is~~ being heated. The mixture set to a solid in cold but melted on heating. The mass was gradually heated to 160°C. and kept at this temperature for 4 hours. After 1 1/2 hours a brown solid began separating and at the end of 4 hours the reaction mixture was in the form of a brown coloured solid. It was diluted after cooling with 200 c.c. of water and the mixture boiled to break the solid and finally cooled in a freezing mixture. The light brown aminosulphonic acid which separated was filtered and recrystallised from 200 c.c. boiling water after decolourising with norit charcoal. The colourless needles which separated on cooling were collected and dried (6.8 g.) and a further crop of crystals was recovered by concentrating the mother liquor to 60 c.c. (1 g.). The filtrate after separating the crude sulphonic acid was made alkaline with 50% caustic soda solution when the acid sulphate of the unreacted amine gave the free amine which was then ether-extracted. The ether extract was washed free from

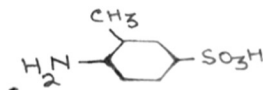
alkali, dried over unhydrous sodium sulphate and taken down to dryness, when 5.8 g. of the amine was recovered.

Sulphonation of Cumidine.

Technical cumidine (Eastman Kodak Co.) was distilled at 210-234°C. Most of it distilled between 220-230°C. It distilled as a colourless liquid, but darkened on keeping to reddish yellow. Fuming sulphuric acid (20%, 23.7 c.c.) was gradually added to distilled cumidine (15 g.) kept in a 100-c.c. 3-necked flask fitted with a mechanical stirrer and externally cooled in ice. The mass was then gradually heated in boiling water bath and treated at this temperature for 2 hours. The reaction mixture was diluted with 50 c.c. ice cold water (5°C.), when a light brown solid separated and left over night in the refrigerator. The sulphonic acid was collected and recrystallised from boiling water (800 c.c.) after noritting. On cooling the sulphonic acid separated as small needles, which were collected and dried (4 g.). A further crop of crystals was collected by concentrating the mother liquor to 200 c.c. (1.7 g.). The unreacted cumidine was recovered by making the filtrate after separating the crude sulphonic acid alkaline with excess of caustic soda and extracting with ether. 1.9 g. Of cumidine were thus recovered.

Sulphonation of o-toluidine.

o-Toluidine-5-sulphonic acid:



o-Toluidine was sulphonated by fuming sulphuric acid containing 20% SO_3 at 180°C . (cf. Schultz and Lucas, J. Amer. Chem. Soc., 1927, 49, 298). Fuming sulphuric acid (20%, 2 mols, 19.4 c.c.) was gradually added to o-toluidine (20 g.) kept stirred up in a 100-c.c. 3-necked flask fitted with a mechanical stirrer and externally cooled in ice. After the addition of acid, the sulphonation mixture was gradually heated to 180°C . and heated for 8 hours. After cooling the thick brown paste was diluted with 50 c.c. cold water (5°C .), when a white solid separated. The mixture was kept over a night in the refrigerator and the sulphonic acid was collected and recrystallised after neutralising from boiling water (250 c.c.). Colourless needles separated on cooling, which were collected and dried (17.7 g.). By concentrating the mother liquor to 50 c.c. a further crop of crystals was collected (2.3 g.). The aqueous solution after separating the sulphonic acid was made alkaline with caustic soda and some of the unreacted o-toluidine which separated was recovered by extracting with ether (1.9 g.).

Synthesis of new wetting agents:

Preparation of the fatty acid chloride: The acid was treated with molecular proportion of phosphorus trichloride (3 mols) on boiling water bath for 30 minutes, in a round bottomed flask fitted with an air condenser and a calcium chloride tube. The upper layer of the acid chloride was decanted off from the lower layer of phosphorus acid, and used without further purification for condensing with aryl-amine sulphonic acids. Freshly prepared fatty acid chlorides were used in the preparation of the condensates. Lauryl and oleyl chlorides and chlorides of fatty acids from coconut, mowhra, cotton seed and groundnut oils were ^{similarly} prepared and used.

(a) Derivatives of lauric acid:

Lauryl-p-anisidide-3-sodium sulphonate (I): Lauryl chloride (1 mol), p-anisidine-3-sulphonic acid (1 mol) and pyridine (10 c.c.) were mixed in a round bottomed flask fitted with an air condenser and heated in an oil bath at 140-150°C. for 2 hours with intermittent shaking. The reaction mixture, after cooling, was dissolved in water, and neutralised to phenolphthalein with 10% caustic soda solution. It was heated on steam bath to remove pyridine and finally taken down to dryness. The dry mass was powdered and extracted with hot ethyl acetate, and the wetting agent

recovered by distilling off the solvent. It was then dried on steam bath and finally in oven at 100°C. and then kept over calcium chloride in a desiccator. The pure compound was a light brown gritty powder (Found:Na, 5.7; S, 7.7. $C_{19}H_{30}O_5NSNa$ requires Na, 5.7%; S, 7.9%).

Lauryl-p-anisidide-2-sodium sulphonate (III): The compound was prepared as in (I). The reaction mixture was dark coloured and on diluting with water gave a dark coloured precipitate. On neutralising with caustic soda solution, it gave a dark solution which was heated on steam bath to remove pyridine and finally taken down to dryness. The crude wetting agent was purified by extraction with ethyl acetate. The pure compound was cream coloured gritty powder (Found: Na, 5.8; S, 7.8. $C_{19}H_{30}O_5NSNa$ requires Na, 5.7%; S, 7.9%).

Lauryl-p-phenetidide-3-sodium sulphonate (V) and Lauryl-p-phenetidide-2-sodium sulphonate (VII): These compounds were prepared as in (I) and purified by redistilled ethyl acetate. Compound (V) was cream coloured solid (Found: Na, 5.6; S, 7.4. $C_{20}H_{32}O_5NSNa$ requires Na, 5.5%; S, 7.6%). The reaction mixture in the case of compound (VII) behaved as in compound (III), forming insoluble precipitate on diluting with water. It dissolved on neutralising in caustic soda solution. It was further worked up as in compound (III).

The pure compound was a brown substance (Found: Na, 5.7; S, 7.5. $C_{20}H_{32}O_5NSNa$ requires Na, 5.5%; S, 7.6%).

Lauryl-o-toluidide-4-sodium sulphonate (XVIII) and Lauryl-o-toluidide-5-sodium sulphonate (XXI): In either case the reaction is almost instantaneous. After mixing the reacting substance the mixture became hot. The final reaction mixtures were in the form of a reddish yellow oil. Both the compounds were purified with ethyl acetate. Compound (XVIII) was a cream coloured gritty powder (Found: Na, 5.6; S, 8.0. $C_{19}H_{30}O_4NSNa$ requires Na, 5.9%, S, 8.2%). Compound (XXI) was a brown sticky substance (Found: Na, 5.8; S, 8.1. $C_{19}H_{30}O_4NSNa$ requires Na, 5.9%; S, 8.2%).

Lauryl-m-4-xylylidide-6-sodium sulphonate (XXIV) and Lauryl-m-4-xylylidide-5-sodium sulphonate (XXVII): Both compounds had to be purified by Soxhlet extraction with ethyl acetate due to their low solubilities in the solvent. Compound (XXIV) can also be purified by first washing with hot benzene, extracting with hot absolute alcohol. It was a crisp whitish powder (Found: Na, 5.5; S, 8.1. $C_{20}H_{32}O_4NSNa$ requires Na, 5.7%; S, 7.9%). Compound (XXVII) was sticky cream coloured paste (Found: Na, 5.8; S, 8.0. $C_{20}H_{32}O_4NSNa$ requires Na, 5.7%; S, 7.9%).

Lauryl cumidide sodium sulphonate (XXX): The compound was purified with ethyl acetate. It was yellowish brown powder (Found: Na, 5.5; S, 7.4. $C_{21}H_{34}O_4NSNa$ requires Na, 5.5%; S, 7.6%).

(b) Derivatives of oleic acid:

Oleyl chloride was prepared by the general method described previously.

Oleyl-p-anisidide-3-sodium sulphonate (II) and Oleyl-p-phenetidide-3-sodium sulphonate (VI): Compound (II) was a hygroscopic brown solid. It was purified by extraction with ethyl acetate in a soxhlet (Found: Na, 4.7%. $C_{25}H_{40}O_5NSNa$ requires Na, 4.7%). Compound (VI) was a reddish brown sticky hygroscopic solid (Found: Na, 4.8. $C_{26}H_{42}O_5NSNa$ requires 4.6%).

Oleyl-p-anisidide-2-sodium sulphonate (IV) and Oleyl-p-phenetidide-2-sodium sulphonate (VIII): These behave as the corresponding lauryl derivatives and were purified by ethyl acetate. Compound (IV) was a light brown solid like (III) (Found: Na, 4.7%). Compound (VIII) was dark brown sticky substance (Found Na, 4.7%).

Oleyl-o-toluidide-4-sodium sulphonate (XIX) and Oleyl-o-toluidide-5-sodium sulphonate (XXII): The reaction mixture in either case was deep red in colour. Compound (XIX) was first purified with absolute alcohol and finally by

extraction with ethyl acetate in a soxhlet. It was^a/brownish, sticky substance (Found: Na, 4.8. $C_{25}H_{40}O_4NSNa$ requires Na, 4.9%). Compound (XXII) was also purified from ethyl acetate. It was light brown powder (Found: Na, 5.0%).

Oleyl-m-4-xylylidide-6-sodium sulphonate (XXV) and Oleyl-m-4-xylylidide-5-sodium sulphonate (XXVIII): Compound (XXVIII) was purified by ethyl acetate and compound (XXV) by dioxan. Compound (XXV) was a reddish brown hygroscopic powder (Found: Na, 4.8, S, 6.5. $C_{26}H_{42}O_4NSNa$ requires Na, 4.7%; S, 6.6%). Compound (XXVIII) was transparent viscous jelly (Found: Na, 4.6%).

Oleylcumidide sodium sulphonate (XXXI). The reaction mixture was deep yellow in colour. It was purified by extraction with ethyl acetate in a soxhlet. It was a yellowish brown sticky product (Found: Na, 4.5. $C_{27}H_{44}O_4NSNa$ requires Na, 4.6%).

(c) Derivatives of coconut oil fatty acids:

The mixed fatty acids from coconut oil were obtained by saponifying the oil with alcoholic caustic soda solution and breaking the soap by excess of dilute sulphuric acid. The fatty acids which separated were extracted with ether, washed free from acid, dried over anhydrous sodium sulphate and used in the preparing the derivatives. The mean molecular

weight of the mixed fatty acids was found to be 200 and the acid chloride was accordingly prepared by treatment with phosphorus trichloride on a water bath as in preparation of lauryl and oleyl chlorides.

Derivative from p-toluidine-2-sulphonic acid (XIV):

The mixed fatty acid chloride and the arylamine sulphonic acid were mixed in molecular proportions, and refluxed together with pyridine as usual at 140-150°C. for two hours. The deep red reaction mixture was diluted with water, neutralised with 10% caustic soda solution and worked up as usual. It was purified by first washing with hot alcohol and finally by extraction with ethyl acetate. It was a cream coloured gritty powder (Found: Na, 6.0. Theoretical Na, 5.9%).

Derivatives from o-toluidine-4-sulphonic acid (XX) and o-toluidine-5-sulphonic acid (XXIII): Both the compounds were purified with ethyl acetate. Compound XX was a light brown powder (Found Na, 6.1%). Compound XXIII was a cream coloured powder (Found: Na, 5.8%).

Derivatives from m-4-xylylidine-6-sulphonic acid (XXVI) and m-4-xylylidine-5-sulphonic acid (XXIX) In either case the reaction mixture was deep yellow in colour. Compound (XXVI) was prepared in pure state by extraction with ethyl acetate while in the case of compound (XXIX) dioxan was used in

purification. Compound (XXVI) was a light brown powder (Found: Na, 5.8%. Theoretical Na, 5.7%). Compound (XXIX) was dark brown jelly (Found: Na, 5.6%).

(d) Derivatives from p-toluidine-2-sulphonic acid and fatty acid chlorides: p-Toluidine-2-sulphonic acid was condensed with myristyl, palmityl and stearyl chlorides and the chlorides of mixed fatty acids obtained from coconut, cotton seed, groundnut and mowhra oils to give the corresponding condensates. Myristyl, palmityl and stearyl chlorides were prepared in the usual manner and the acid chloride was decanted off from the phosphorus acid while hot, as the chlorides solidified on cooling. The acid chlorides thus prepared were condensed with equivalent amount of p-toluidine-2-sulphonic acid by refluxing ^{with} pyridine at 140-150°C. for four hours. The reaction mixture after neutralising with 10% caustic soda solution was heated on steam bath to remove pyridine and finally taken down to dryness. The stearyl and palmityl derivatives were sparingly soluble in most of the solvents, except alcohol. They were therefore purified by extracting with hot absolute alcohol, but the purified products gave slightly higher sodium on analysis. The myristyl compound was purified with ethyl acetate. The stearyl-p-toluidine-2-sodium sulphonate (XII) was a reddish yellow gritty powder (Found: Na, 5.2. $C_{25}H_{42}O_4NSNa$ requires Na, 5.0%). Palmityl-p-toluidide-2-sodium sulphonate (XI)

was a yellow gritty powder (Found: Na, 5.5. $C_{23}H_{38}O_4NSNa$ requires Na, 5.2%). Myristyl-p-toluidide-2-sodium sulphonate (X) was brownish powder (Found: Na, 5.5. $C_{21}H_{34}O_4NSNa$ requires Na, 5.5%).

Cocoanut, cotton seed, groundnut and mowhra oils were saponified with alcoholic caustic potash and the soaps were decomposed by boiling with excess of dilute sulphonic acid. The fatty acids were extracted with ether, the ether extract after washing free from acid and drying over unhydrous sodium sulphate was distilled off. The mixed fatty acids were then dissolved in neutral alcohol and titrated with 0.1N caustic soda solution and the mean molecular weights were determined. The mean molecular weights of the mixed fatty acids from cocoanut, cotton seed, groundnut and mowhra oils were found to be 200, 283.5, 282 and 296 respectively. These were treated with phosphorus trichloride to give the corresponding acid chlorides which were subsequently condensed with p-toluidine-2-sulphonic acid. The acid chloride and p-toluidine-2-sulphonic acid were taken in molecular proportions and condensed in the usual way. The crude wetting agents were purified from absolute alcohol and gave slightly higher value for sodium

Compound (XIV) condensate from mixed fatty acids from cocoanut oil (Found: Na, 6.0. Calc. Na, 5.9%).

Compound (XV) condensate from mixed fatty acids from
cotton seed oil (Found: Na, 5.3. Calc. Na, 5.0%).

Compound (XVI) condensate from mixed fatty acids from
groundnut oil (Found: Na, 5.2. Calc. Na, 5.0%).

Compound (XVII) condensate from mixed fatty acids from
mowhra oil (Found: Na, 5.0. Calc. Na, 4.7%).

Properties of the new synthetic wetting agents.

Qualitative stability tests.

(a) Stability towards alkali. A solution of the wetting agent (2%, 5 c.c.) and caustic soda solution (10%, 5 c.c.) were mixed in a test tube and the change noted in the cold and on boiling.

Compound (V) gave a clear solution in cold but oily drops departed on boiling. Compound (VI) gave a curdy precipitate in cold. Except for these compounds, the rest gave clear solutions both in cold and on boiling.

(b) Stability towards mineral acids: A solution of the wetting agent (2%, 5 c.c.) was mixed with sulphuric acid (5%, 5 c.c.) and the change noted in cold and boiling.

Compounds (I), (XVIII), (XIV), (XXIII), (XXIV), (X) and (IX) were stable both in cold and on boiling. Compounds (II), (XI), (V) and (XIII) gave turbid solutions in cold, but became clear after boiling. Compounds (III), (IV), (XVII), (XXII), (XXV), (XXVI) and (XXXI) were stable in cold, but

on boiling gave milky solutions, or oily drops in certain cases. Compounds (VI), (VII), (VIII), (XII), (XV), (XVI), (XIX), (XX), (XXI), (XXVII), (XXVIII), (XXIX), (XXX) decomposed in cold giving turbid solutions or curdy precipitates, and there was no alteration on heating.

(c) Stability to hard water: On treating 5 c.c. of 0.5% solution of wetting agent with 5 c.c. of a 1% solution of calcium chloride, (IX), (XVII) and (XIII) remained quite clear; (I), (X), (XIV), (XXII), (XXIII), (XXIV), (XXV), (XXVIII), (XXIX) and (XXX) were slightly turbid, while the others gave curdy precipitates.

Properties of the new synthetic wetting agents:

Determination of wetting power:

(a) Herbig number: The Herbig number tests were carried out in the modified Herbig apparatus (Forster, Uppal and Venkataraman, J. Soc. Dyers Col., 1938, 54, 465). This apparatus is a modification of the Evan's apparatus (ibid., 1935, 51, 233). The Herbig machine consists of a screwed spindle which is attached to the main frame of the machine through an axle in such a way that it can be rotated in a vertical position, when centrifuging the yarn. On the top of the spindle a hook of steel is attached by means of nuts. The spindle rotates by means of a mechanical friction clutch,

one component of which is coupled to a single phase A.C. 1/8 H.P. motor with a reversing switch.

To maintain a constant number of revolutions of the spindle during centrifuging, there is a nut which moves along the length of the spindle either up or down. At one end of the nut there is a projection which, when the nut is moving up, pushes a knob of the switch which is attached to the main frame at the top. This breaks the circuit of the electric motor and the spindle stops. When the spindle is in this position, a hank is attached to the hook of the spindle and the main switch of the electric motor is switched off, as the switch at the top cuts off the electric current only when the knob is pressed. The lower component of the friction clutch is then detached by means of a handle attached to it and is kept in this position by means of an iron strip. This iron strip is attached to another strip of iron (fitted to the main frame by means of a pin so that it can move in the vertical plane only). The lower end of the strip holds the clutch in position, while the top end is kept pulled by means of a spring attached to the main frame. After the clutch is detached, the spindle is brought to a horizontal position by means of a lever, so that the hank (attached to the hook) can dip in the solution to be tested. After the hank has been dipped for the requisite length of time, it is

brought out of the solution, the weight attached to the hank removed, and the motor started. This time the motor should rotate in a direction which will bring the nut ~~moving~~ along the spindle down. The spindle is then pressed into the vertical position which pushes in iron strip holding the lower component of the friction clutch, and the spindle starts rotating. The spindle is automatically stopped by means of the strip attached to the moving nut which disengages the lower component of the clutch by pushing it down. The main switch is then switched off.

The temperature of the solution to be tested can be controlled and also raised to 97°C. by means of a thermostat in which the test tube containing the solution is held. In carrying out the test as described by Evans (loc. cit.) approximately 0.5 g. of hanks of 20's grey yarn, free from size and conditioned at room temperature were used. A 10 g. weight was employed to ^{keep} the yarn weighted in the solution which was contained in a test tube, care being taken to ensure complete immersion of the whole length of the yarn. ~~The test~~ In all cases the period of immersion was 30 secs. The test tube was held in the thermostat. Five hanks were used for each test, and three such readings were taken in each case as these were generally found to lead to a representative average result. The "Herbig number" is the weight of liquor

absorbed by 100 g. of the textile material.

For standardising the machine from time to time and after overhaul 0.25% solution of Aerosol OT which is claimed to be a 100% pure wetting agent by the American Cyanamide Chemical Corporation is taken and its Herbig number determined, at 30°C. At 0.25% concentration the Herbig number is 70. The quality of the yarn to be employed should be the same throughout. An error of 2% in Herbig number is allowed.

The Hernig number tests were carried out in the modified Herbig apparatus with 0.25, 0.15, 0.10, 0.075 and 0.05% solutions of the wetting agents at 30°C. The results are recorded in Table I.

Table I

Compound	Herbig number at 30°C.				
	% Concentration of solution				
	0.25	0.15	0.1	0.075	0.05
I	57.0	54.8	50.6	49.7	44.2
II	54.7	54.2	50.4	44.4	42.9
III	62.3	59.0	56.1	52.9	48.7
IV	56.2	52.5	41.7	37.5	30.0
V	58.0	55.5	54.2	52.9	51.7
VI	55.3	53.7	50.5	48.4	43.1
VII	58.4	55.8	52.1	50.2	45.7
VIII	53.2	47.3	40.1	34.9	29.2

Table I contd.

COMPOUND	Herbig number at 30°C.				
	% Concentration of solution				
	0.25	0.15	0.1	0.075	0.05
IX	63.0	61.7	58.4	55.2	51.2
X	57.3	52.3	49.7	46.9	43.8
XI	35.9	32.6	27.7	27.1	23.0
XII	22.3	21.6	19.5	18.9	18.8
XIII	52.5	50.5	44.6	42.2	36.4
XIV	57.9	55.9	52.1	48.6	42.0
XV	45.3	35.8	28.9	26.1	21.6
XVI	41.2	33.7	29.9	24.0	20.7
XVII	44.3	39.7	35.5	33.1	30.6
XVIII	69.7	68.0	67.6	65.4	62.0
XIX	54.1	50.1	42.7	39.5	33.5
XX	59.8	55.5	48.6	45.4	40.5
*XXI	62.3	60.1	56.6	53.9	51.5
XXII	55.0	49.1	45.7	40.5	34.8
XXIII	61.8	58.6	52.6	43.3	36.6
XXIV	57.2	58.9	55.0	53.7	51.7
XXV	41.8	40.2	38.7	37.2	34.1
XXVI	56.6	54.6	49.4	44.2	40.3
XXVII	62.1	59.9	58.2	54.4	48.5
XXVIII	56.2	52.0	48.5	46.1	43.6

Table I contd.

Compound	Herbig number at 30°C.				
	% Concentration of solution				
	0.25	0.15	0.1	0.075	0.05
XXIX	60.5	53.9	51.4	42.2	41.1
XXX	64.2	59.8	56.5	51.2	46.7
XXXI	53.5	50.7	45.7	43.6	38.5
XXXII	60.2	59.0	56.1	54.0	50.9
XXXIII	51.0	49.0	46.7	45.2	41.7
Product Y	58.5	56.5	54.7	53.7	52.0

Lauryl-o-toluidide-4-sodium sulphonate (XVIII) gave the highest Herbig number at all concentrations. The other wetting agents ranged themselves as follows according to decreasing Herbig number at the stated concentrations:

At 0.25%:- (XXX), (IX), (XXI), (III), (XXVII), (XXIII), (XXIX), (XXXII), (XX), Product Y, (VII), (V), (XIV), (X), (XXIV), (I), (XXVI), (XXVIII), (IV), (VI), (XXII), (II), (XXXIV), (XIX), (XXXI), (VIII), (XIII), (XXXIII), (XV), (XVII), (XXV), (XVI), (XI), (XII).

At 0.15%:- (IX), (XXI), (XXVII), (XXX), (XXXII), (III), (XXIV), (XXIII), Product Y, (XIV), (VII), (V), (XX), (I), (XXVI), (II), (XXIX), (VI), (IV), (X), (XXVIII), (XXXI), (XIII), (XIX), (XXII), (XXXIII), (VIII), (XXV), (XVII), (XV), (XVI), (XI), (XII).

At 0.1%+- (IX), (XXVII), (XXI), (XXX), (III), (XXXII), (XXIV),
Product Y, (V), (XXIII), (XXXII), (VII), (XIV),
(XXIX), (VI), (II), (X), (XXVI), (XX), (XXVIII),
(XXXIII), (XXII), (XXXI), (XIII), (XIX), (IV),
(VIII), (XXV), (XVII), (XVI), (XV), (XI), (XII).

At 0.075%+- (IX), (XXVII), (XXXII), (XXI), Product Y, (XXIV),
(III), (V), (XXX), (VII), (I), (XIV), (VI), (X),
(XXVIII), (XX), (XXXIII), (II), (XXVI), (XXXI),
(XXIII), (XXIX), (XIII), (XXII), (XIX), (IV), (XXV),
(VIII), (XVII), (XI), (XV), (XVI), (XII).

At 0.05%:- Product Y, (XXIV), (V), (XXI), (IX), (XXXII), (III),
(XXVII), (XXX), (VII), (I), (X), (XXVIII), (VI),
(II), (XIV), (XXXIII), (XXIX), (XXI), (XX), (XXVI),
(XXXI), (XIII), (XXII), (XXV), (XIX), (XVII), (IV),
(VIII), (XI), (XV), (XVI), (XII).

* Herbig number determination at 60°C.

Lauryl-p-toluidide-2-sodium sulphonate stood second at concentrations of 0.15, 0.1, and 0.075%, and Product Y at 0.05%.

From Table I it will be seen that lauric acid compounds were consistently better than the corresponding oleic acid derivatives as judged by Herbig number at all concentrations. Thus compounds (I), (III), (V), (VII), (XVIII), (XXI), (XXIV), and (XXVII) gave higher Herbig number than (II), (IV), (VI), (VIII), (XIX), (XXII), (XXV) and (XXVIII) respectively.

Although no definite conclusion could be drawn about the position of the sulphonic acid group with respect to the

amino group in the benzene ring, it was found that in majority of cases m-orientation of the sulphonic and amino groups in the lauric acid compounds gave better wetting agents than o-orientation, while in oleic acid compounds the o-compounds were better wetting agents. Thus lauric acid compounds of p-anisidine-2-sulphonic acid and p-phenetidine-2-sulphonic acid were better than the corresponding derivatives of p-anisidine-3-sulphonic acid and p-phenetidine-3-sulphonic acid. Lauryl-m-4-xylylidide-5-sodium sulphonate, however, was better than the o-6-sodium sulphonate at 0.25% and 0.15%, but in more dilute solutions the m-compound was again better than the o-compound. The oleic acid derivatives of p-anisidine and p-phenetidine-3-sulphonic acids were better than the corresponding condensates with m-sulphonic acids. Similarly in the case of m-4-xylylidine sulphonic acids, compound from m-4-xylylidine-5-sulphonic acid was better than the m-4-xylylidine-6-sulphonic acid. Incidentally it may be mentioned that these results confirm the observations made earlier with toluidine sulphonic acids (Shirolkar and Venkataraman, J. Soc. Dyers Col., 1941, 57, 44).

When lauric acid was condensed with o-toluidine-4-sulphonic acid (amino group m- to the sulphonic group) and o-toluidine-5-sulphonic acid (amino group o- to the sulphonic group), the compound in which the amino and sulphonic groups

were in the m- position was better wetting agent as judged by Herbig number than the p compound, but when oleic acid was condensed with the same sulphonic acids, the reverse was found to be the case. In the case of compounds from mixed fatty acids from cocconut oil at 0.25, 0.15 and 0.1% concentrations the p-compounds gave higher Herbig number, while at 0.075 and 0.05% concentrations the m-compound was better.

On comparing lauryl-p-anisidide-2-sodium sulphonate (III) and the corresponding phenetidine compound (VII) with laurylanilide-m-sodium sulphonate (ibid.) it was found that the introduction of methoxy and ethoxy groups improved the wetting power in terms of Herbig number. The oleyl derivatives p-alkoxyanilidide-m-sulphonic acid were also better than oleyl-anilide-m-sodium sulphonate (Uppal and Venkataraman, J. Soc. Dyers Col., 1939, 55, 125) at 0.25% concentration, although at 0.1% the latter had higher wetting power. In the lauryl derivative of orthanilic acid (Shirolkar and Venkataraman, (loc. cit.) C-methoxylation made little change in the wetting power, but oleyl derivatives of alkoxy aniline had again higher wetting power. Introduction of C-alkoxy group in derivatives of arylamine sulphonic acids gave better wetting agents.

It will be of interest to compare these compounds with lauryl and oleyl derivatives of p-toluidine-2- and -3- sulphonic

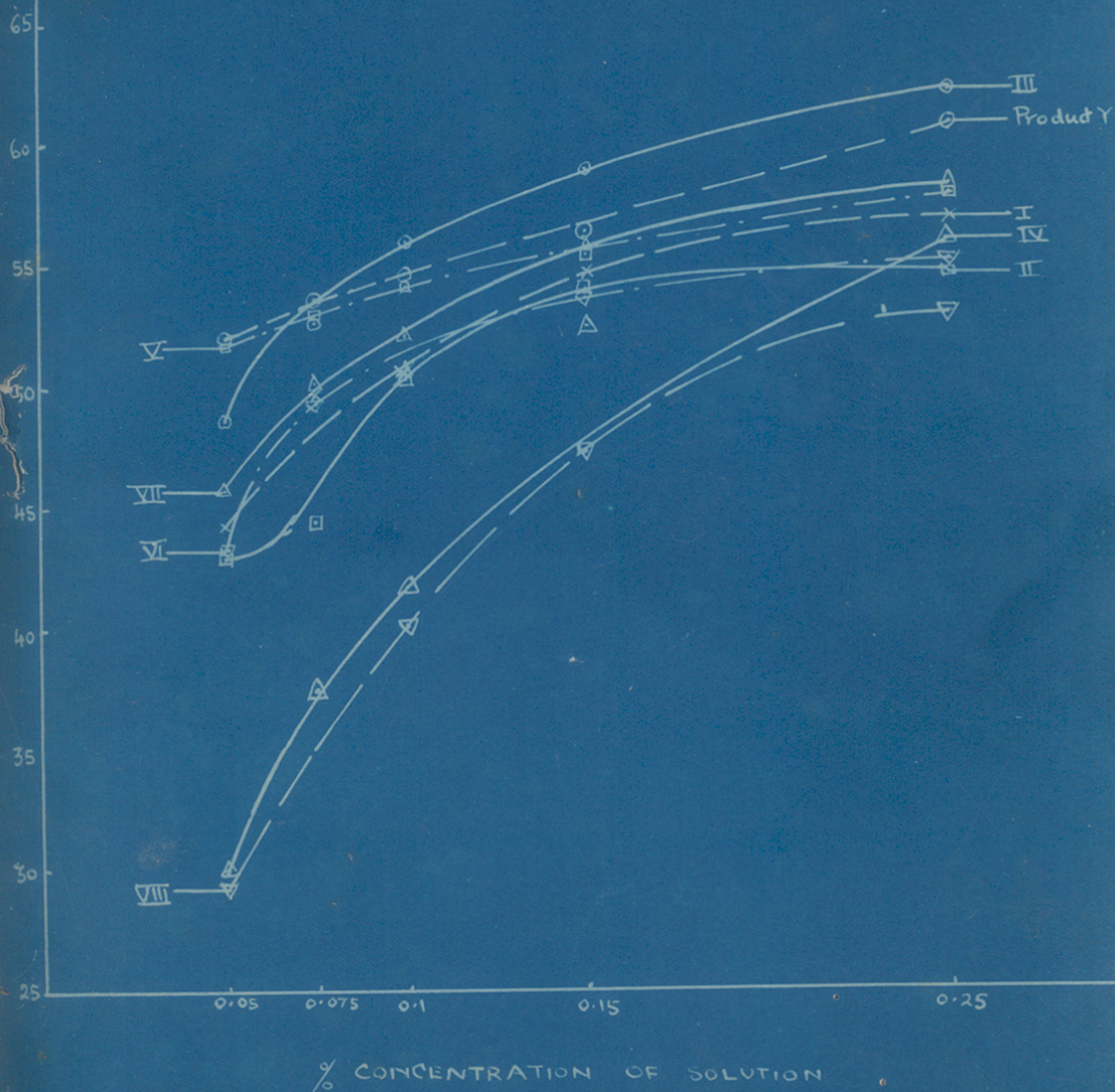


Fig. I

Wetting power of C-alkoxyanilides.

acids (ibid.) to note the effect of substitution of C-alkoxy group in place of C-alkyl group. Except for lauryl-p-toluidide-2-sodium sulphonate which was better than the corresponding p-anisidide and p-phenetidides, C-alkoxy substitution gave compounds having higher wetting power. Thus lauryl and oleyl-p-anisidide-3-sodium sulphonate and oleyl-p-anisidide-2-sodium sulphonate and the corresponding phenetidine compounds gave higher Herbig numbers than the analogous p-toluidides.

Comparing p-anisidine and p-phenetidine compounds (Fig. I), it seemed that increase in the length of the C-alkoxy group gave in a majority of cases poorer wetting agents. Thus, lauryl and oleyl p-anisidide-2-sodium sulphonate (III) and (IV) were better than the corresponding p-phenetidides (VII) and (VIII). The lauric acid compound from p-phenetidine-3-sulphonic acid was, however, better than the corresponding p-anisidine compound, while the oleic acid derivatives were equally efficient.

In comparison with the outstanding qualities of lauryl-p-toluidide-2-sodium sulphonate (loc. cit.), the series of wetting agents prepared by condensing p-toluidine-2-sulphonic acids with acid chlorides of saturated fatty acids and with acid chlorides of mixed fatty acids from vegetable oils like cocoanut, cotton seed, groundnut and mowhra oils were all

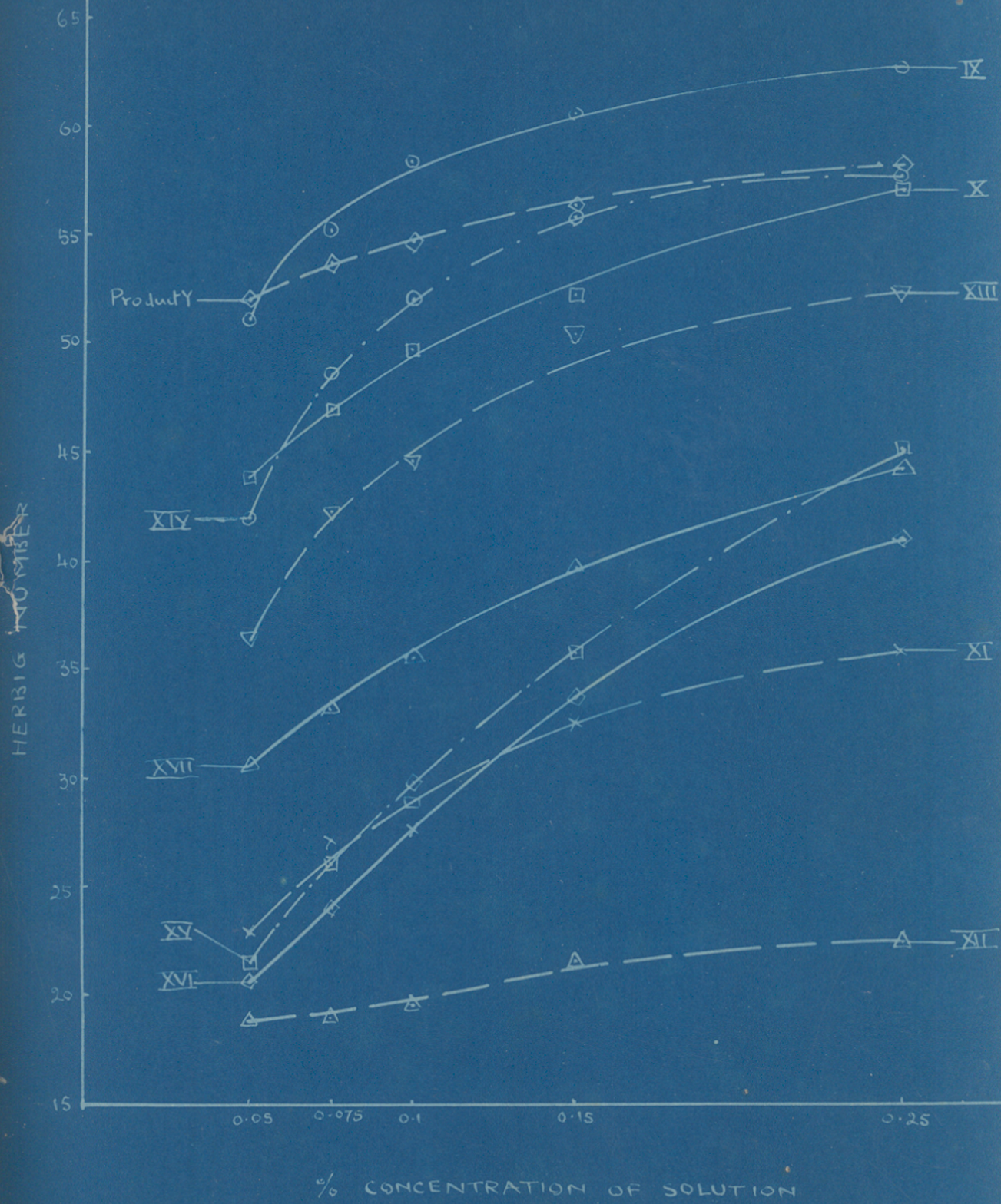


Fig. II

When a liquid is heated, its particles are set in motion and...

WETTING NUMBER

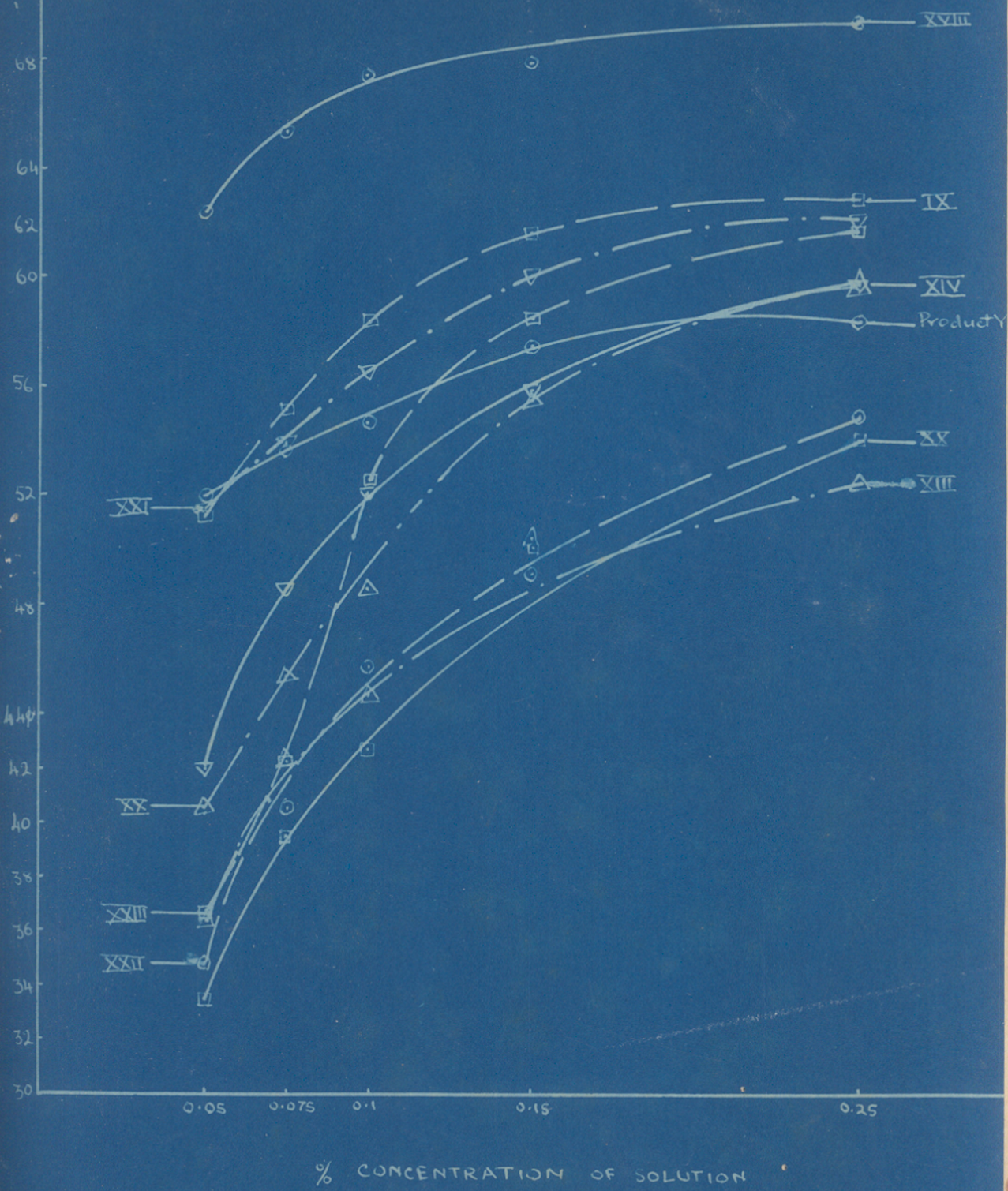


Fig. III

Wetting number of C...

less efficient. As the length of fatty acid chain was increased the Herbig number decreased; palmityl and stearyl p-toluidide-2-sodium sulphonates being only poor wetting agents. Of the compounds from mixed fatty acids, that obtained from mixed fatty acids from cocoanut oil was the best (Fig. II).

By interchanging the positions of the C-alkyl group and sulphonic acid group in lauryl derivative of p-toluidine-3-sulphonic acid, lauryl-o-toluidide-5-sodium sulphonate was obtained and was found to have higher wetting power than the former compound (Fig. III). In oleic acid derivatives the o-toluidide gave higher Herbig number at concentrations above 0.15%, while the p-toluidide was better in more dilute solutions.

In lauryl-o-toluidide-4-sodium sulphonate (XVIII) the carboxylamide group and sulphonic groups were in m- position to each other as in lauryl-p-toluidide-2-sodium sulphonate, while the C-alkyl group was shifted to the o-position to the amino group. By this reorientation a much superior wetting was obtained. The drop in Herbig number with the lowering of the agent concentration of the solution was also more gradual than the p-toluidide. The oleyl derivative of o-toluidine-4-sulphonic acid also gave a higher Herbig number at higher concentrations than the p-toluidine-2-sulphonic acid compound, although the latter when condensed with mixed fatty acids from cocoanut oil gave better wetting agents.

No definite conclusion could be drawn about the effect

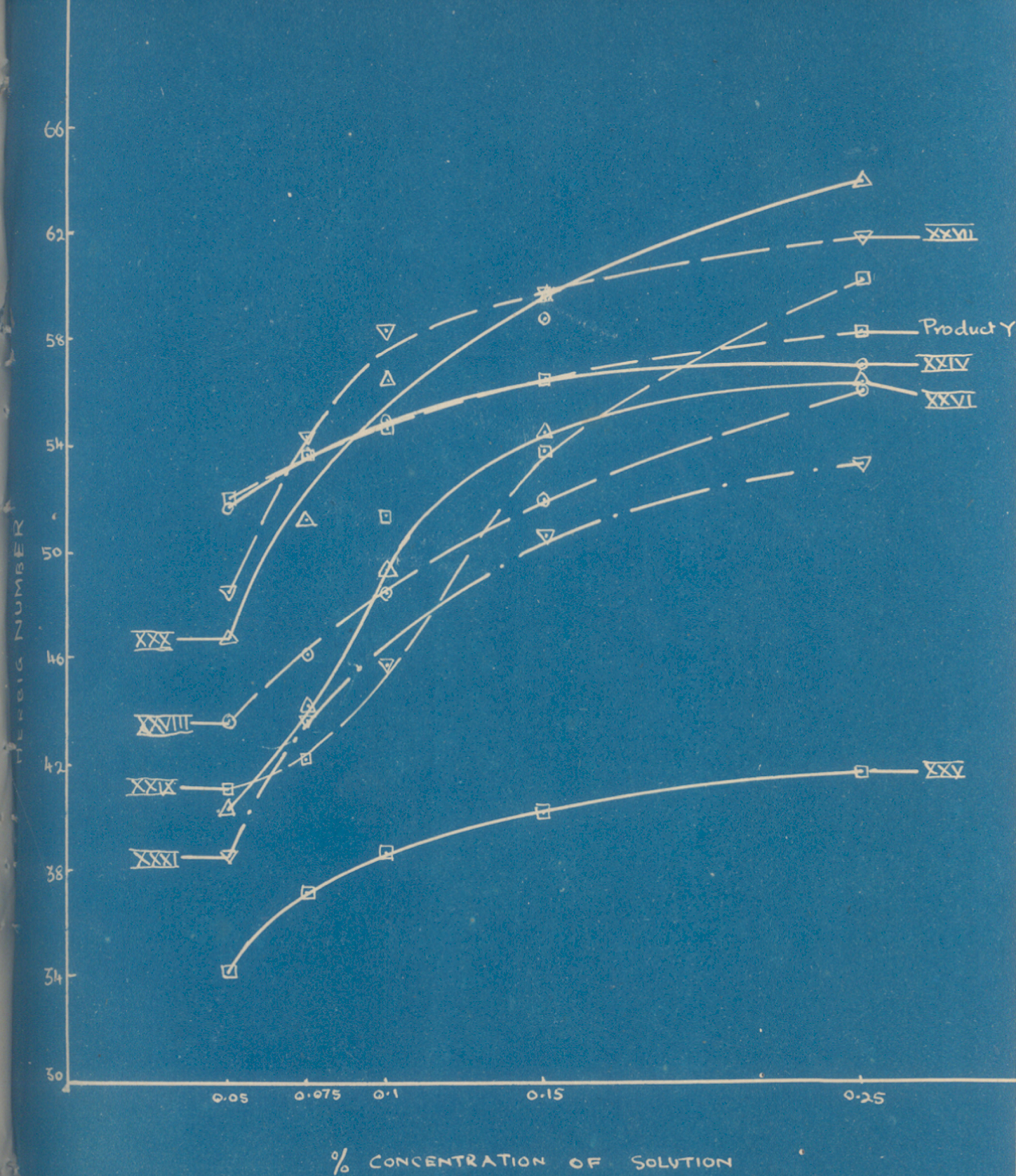


Fig. IV

Wetting angles of *C*-dialkyl and *F*-dialkylamides

of the introduction of C-alkyl group in the benzene ring. When lauric and oleic acids were condensed with metanilic acid and p-toluidine-2-sulphonic acid, compounds containing the C-alkyl group gave higher Herbig number. When, however, orthanilic acid was condensed with lauric acid, it gave a better wetting agent than the corresponding lauric acid derivative from p-toluidine-3-sulphonic acid; while the oleic acid compound of the latter gave higher Herbig number than the corresponding orthanilic acid derivative. An increase in the number of C-methyl groups as in lauryl and oleyl-m-4-xylylidide-6-sodium sulphonates, however, gave poorer wetting agents, these being inferior to the corresponding metanilic and p-toluidine-2-sulphonic acid compounds. The compounds from mixed fatty acids from coconut oil and m-4-xylylidine-6-sulphonic acid behaved similarly. As against the superiority of laurylsodium orthanilate over lauryl-p-toluidide-3-sodium sulphonate, lauric and derivative of m-4-xylylidine-5-sulphonic acid was much better than either of the above compounds. Similarly oleyl-m-4-xylylidine-5-sodium sulphonate gave higher Herbig number than the corresponding orthanilic and p-toluidine-3-sulphonic acid compounds. By increasing the C-alkyl groups further, laurylcumidide sodium sulphonate was obtained. It was a better wetting agent than the dialkyl substituted compound especially at higher concentrations, but was inferior to the monoalkyl

compound. The oleic acid compound from cumidine sulphonic acid was, however, better than the corresponding compound from metanilic, p-toluidine-2-sulphonic, and m-4-xylylidine-6-sulphonic acids (Fig. IV). It appears from the above observations that in lauric acid compounds from metanilic acid, introduction of C-alkyl group increases the Herbig number with the introduction of one C-methyl group and then further increase in C-methyl groups gives inferior wetting agents. In oleic acid compounds the introduction of C-alkyl groups is advantageous and the Herbig number progressively increases with the increase in the C-alkyl groups. (Figs. V and VI)

In laurylsodiumorthanilate introduction of one C-methyl group gave a poorer wetting agent, but a further increase in C-alkyl groups was advantageous as in xylylidine derivatives gave compound (XXVII) which was better than the orthanilic acid compound. Introduction of C-alkyl groups in oleylsodiumorthanilate gave compounds ^{giving} higher Herbig number, which increased with the increase in the number of C-alkyl groups.

(b) Time of sinking: The wetting agents were evaluated by the new test described by Draves and Clarkson (Proc. Amer. Assoc. Text. Chem. Col., 1931, 109; Amer. Dyestuff Rep., 1931, 20, 201) which consisted in finding the time of sinking of a 5 g. unboiled skein of grey 2-ply cotton yarn in a solution of the wetting agent. A 20-g. anchor was attached

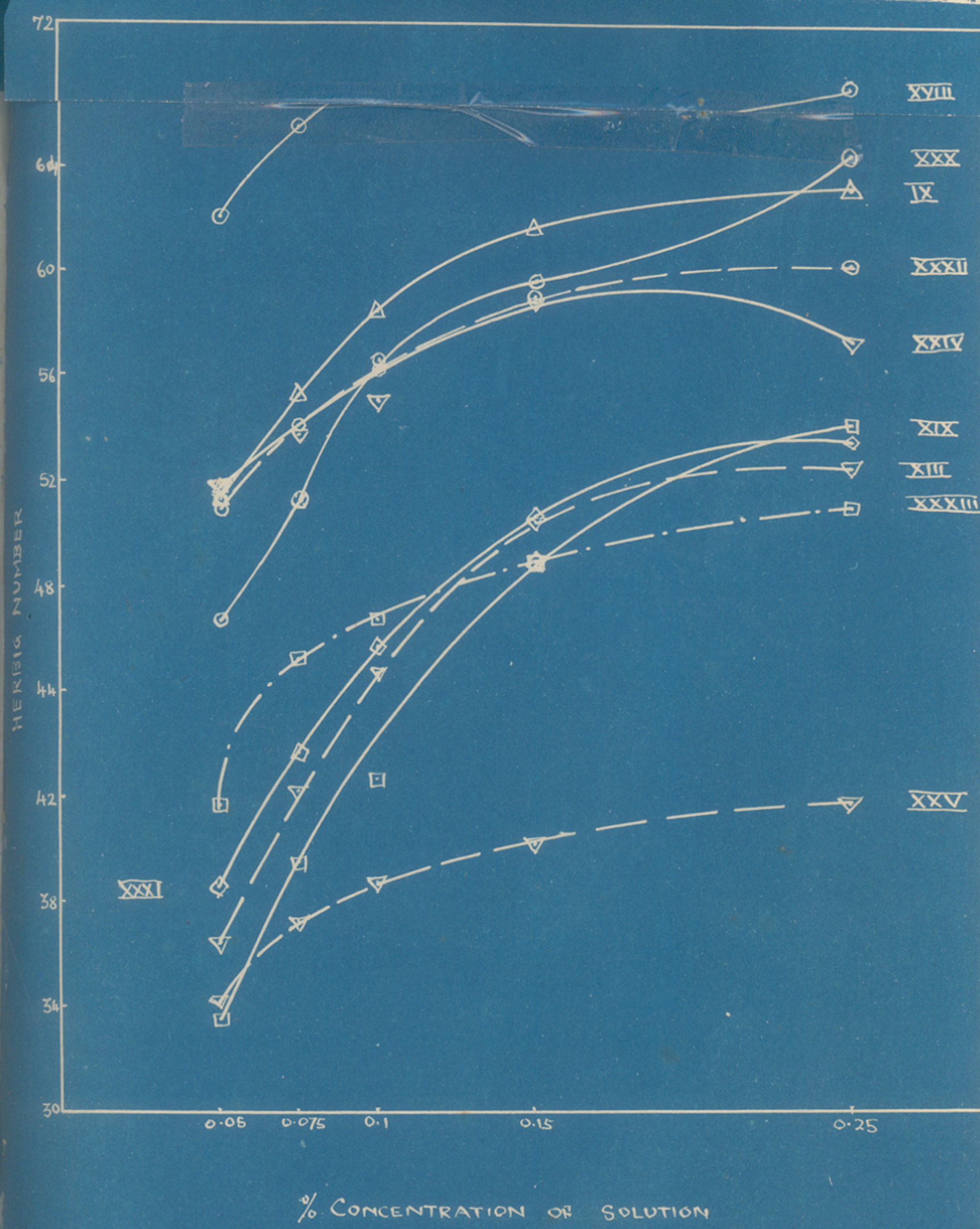


Fig. V

Effect of C-alkyl groups in Lauryl- and Oleylmetanideslides

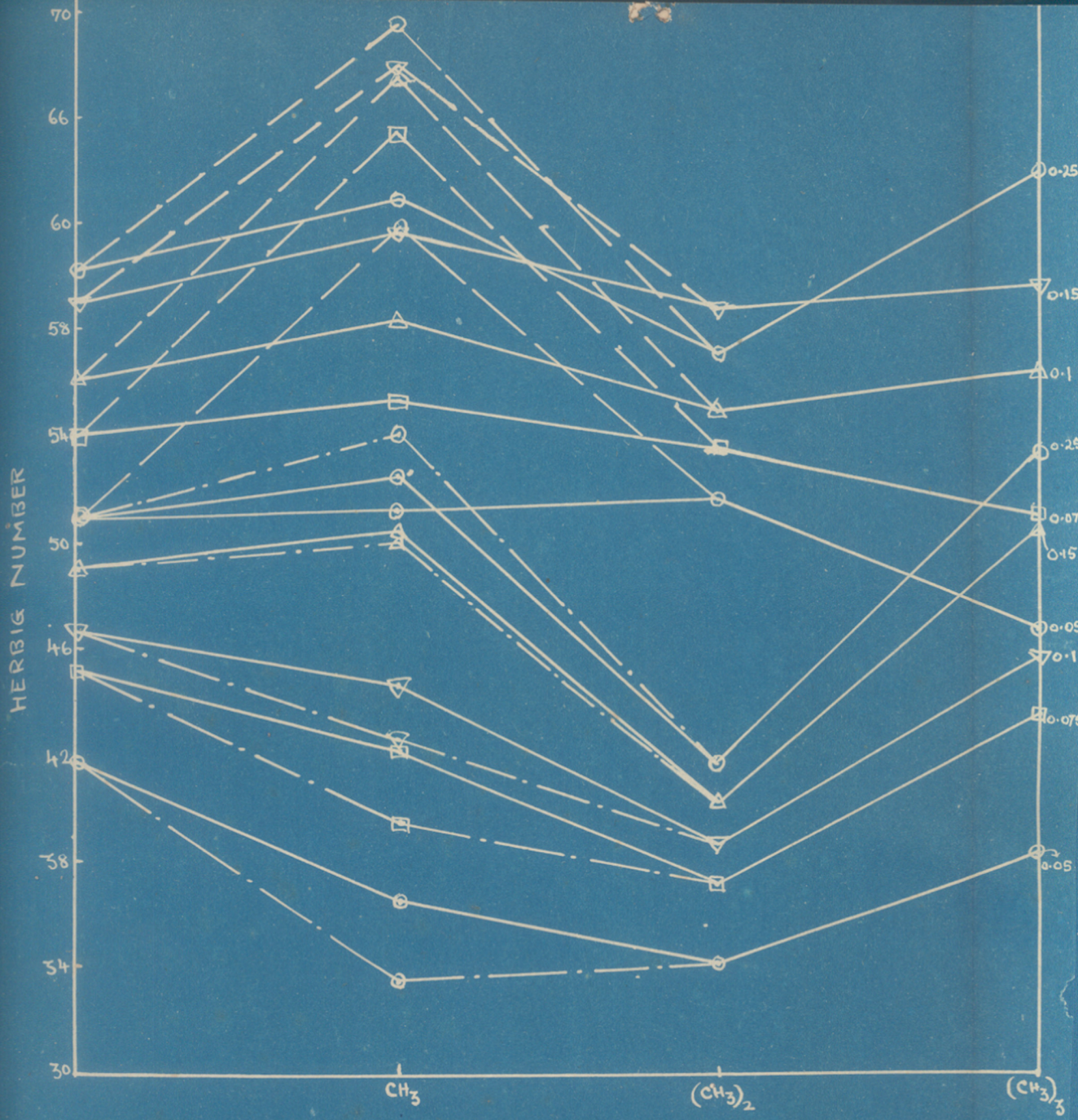


Fig. VI

Relation between wetting power and the number of C-alkyl groups in

by means of a thread 1 inch long to a copper wire hook and lead sinker, having a total weight of 1.5 g. The skein was looped once, the anchor and sinker fastened and the skein cut open at the other end. The whole was then dropped into the solution in a 500 c.c. cylinder and the sinking time noted. Three readings were taken in each case and their mean value was noted. This procedure has been adopted by the American Association of Textile Chemists and Colourists as the standard test for evaluating wetting agents.

The results obtained by the Draves test with 0.1 and 0.05% solutions of the wetting agents at 30°C. are recorded in Table II.

Table II

Compound	<u>Time of sinking in secs. at 30°C.</u>	
	<u>% Concentration of solution</u>	
	0.1	0.05
I	10	41
II	19	40
III	11	30
IV	97	Above 3 mins.
V	6	19
VI	25	66
VII	10	38
VIII	107	Above 3 mins.
IX	6	22

Table II contd.

Compound	<u>Time of sinking in secs. at 30°C.</u>	
	<u>% Concentration of solution</u>	
	0.1	0.05
X	32	96
XI	120	Above 3 mins.
XII	Above 3 mins.	
XIII	12	28
XIV	23	71
XV	Above 3 mins.	Above 3 mins.
XVI	"	"
XVII	96	175
XVIII	10	22
XIX	31	142
XX	36	80
XXI	21	Above 3 mins.
XXII	79	180
XXIII	39	Above 3 mins.
XXIV	8	19
XXV	93	Above 3 mins.
XXVI	35	110
XXVII	7	18
XXVIII	26	64
XXIX	33	83
XXX	41	Above 3 mins.

XXXI

Table II contd.

Compound	Time of sinking in secs. at 30°C.	
	% Concentration of solution	
	0.1	0.05
XXXI	42	84
Product Y (Igepon T)	20	42

The values obtained were not in the same order as the Herbig number at these concentrations.

Compound (XVIII) which gave highest Herbig number at 0.1 and 0.05% concentrations was only fourth in order judged by the time of sinking. Compounds (IX) and (V) were the best at 0.1 concentrations, while compound (XXVII) was the best at 0.05%. The compounds were in the following order of merit at the stated concentrations.

At 0.1%:- (V), ^(IX) (XXVII), (XVIII), XXXIII, I, VII), (XXXII), (II), Product Y, (XXI), (XIV), (VI), (XXVIII), (XIX), (X), (XXIX, XXXIV), (XXVI), (XX), (XXIII), (XXX), (XXXI), (XXII), (XXV), (XVII), (IV), (VIII), (XI), (XV, XII, XVI).

At 0.05%:- (XXVII), (V, XXIV), (XVIII), (III), (XXXIII), (VII), (II), (I), Product Y, (XXXII), (XXVIII), (VI), (XIV), (XX), (XXIX), (XXXI), (X), (XXVI), (XIX), (XVII) (XXII) (IV, VIII, XI, XV, XXIII, XXV, XXX, XXXIV, XII).

Comparing the lauryl and oleyl derivatives of metanilic acid and orthanilic acid (J. Soc. Dyers Col., 1937, 53, 44; ibid. 1939, 55, 125) with C-alkoxy substituted compounds it was found that the new products were better as judged by flotation method, and that phenetidine compounds were slightly better than anisidine compounds.

In the derivatives from p-toluidine-2-sulphonic acid, the lauric acid compound was the best, and the wetting power decreased with increase in length of fatty acid chain. In the mixed fatty acid derivatives the cocoanut oil fatty acid compound was the best, although it was inferior to the lauryl compound.

In all the compounds prepared, those in which the amino and sulphonic groups were in o position to each other were consistently superior to those in which they were in the m position. In the derivatives of o-toluidine-4-sulphonic acid (amino and sulphonic groups in m position to each other) and o-toluidine-5-sulphonic acid (amino and sulphonic groups p- to each other), those compounds in which amino and sulphonic groups were in m position were better wetting agents as shown by the sinking time.

C-Alkyl substitution in the benzene ring in a majority of cases gave better wetting agents. Thus, lauric acid and oleic acid derivatives of p-toluidine-2-sulphonic acid, and

m-4-xylidine-5- and -6-sulphonic acids and oleic acid derivatives from cumidine sulphonic acid were all better than the corresponding derivatives from metanilic and orthanilic acids. Lauryl cumidine sodium sulphate (XXX) and lauryl-p-toluidine-3-sodium sulphate at 0.1% concentration were exceptions. Increase in the number of C-alkyl groups increased the wetting power in some cases, while in others it was reduced.

All the lauric acid compounds were superior to the corresponding oleic acid derivatives.

At 0.1% concentration (XIX) was as good and (V), (XXVII), (XXIV), (XVIII), (XXXII), (I), (VII), (III) and (XXXII) definitely better than Product Y (purified Igepon T), although except for (XXVII), (III), (XVIII) and (XXIV), Product Y gave higher Herbig number than the other compounds at 0.1% concentration. At 0.05% concentration except for (XXXII), all the above mentioned products were again better than Igepon T, whereas the latter was ranked second in Herbig number determination.

(c) Determination of calcium soap dispersion power:

(i) Titration method:(Ramachandran, Uppal and Venkataraman, J. Soc. Dyers Col., 1938, 54, 520). Standard solutions of sodium oleate were prepared by titrating oleic acid in water against standard caustic soda solution, the
The sodium oleate solution used in the following experiment

normality being confirmed by titrating the sodium oleate with hydrochloric acid to a grey neutral point using Hickman and Linstead's ~~ma~~ mixed indicator, i.e. Xylene Cyanol FF and Methyl Orange (Hickman and Linstead, J. Chem. Soc., 1922, 121, 2502); all the titrations in the sequel were carried out with ~~this~~ this indicator. The titration method for the estimation of hard water resisting power consisted in mixing solutions of sodium oleate, auxiliary agent and calcium chloride in a 125-c.c. glass stoppered conical flask, shaking vigorously and filtering the mixture after 5 minutes through a bed of glass wool and Gooch asbestos in a 2 inch open glass funnel. The precipitate was washed thrice with 10 c.c. lots of distilled water and the combined filtrate and washing titrated with N/10 hydrochloric acid. A blank was carried out with the sodium oleate and calcium chloride in the absence of auxiliary agent; the titre of the auxiliary agent with the acid was also separately examined and both the blank values allowed for in calculating the volume of hydrochloric acid required to decompose the oleate in solution. The resistance to hard water was taken to be proportional to the volume of hydrochloric acid, since it would correspond to the amount of sodium and calcium oleate dispersed or held in solution. Preliminary trials showed that the method was best applied to moderately strong solutions of soap and calcium chloride. The sodium oleate solution used in the following experiment

was 2.3%, i.e. N/13.2; 20 c.c. of this solution were exactly equivalent to 25 c.c. of 0.34% i.e. N/16.5 calcium chloride. The blank titre obtained by mixing 20 c.c. of the soap and 25 c.c. of the calcium chloride and filtering was 3.1 c.c. of N/10 hydrochloric acid, presumably representing the solubility of calcium oleate in 75 c.c. of water at room temperature, viz., 29-30°C.

To 20 c.c. of the soap solution, 5 c.c. of 1% auxiliary agent solution were added, followed by 25 c.c. of the calcium chloride solution, and the net values obtained are recorded in Table III. As against the use of 2.5 c.c. and 5 c.c. of 2% solution of the wetting agent, 5 c.c. of 1% solution was used as most of the compounds gave clear solution at 1% concentration, at room temperature (29-30°C.).

Table III

Compound	<u>Net dispersion</u>	<u>Point light method</u>
	<u>Vol. of auxiliary agent solution</u> <u>5 c.c. of 1%</u>	<u>% concentration of calcium chloride solution.</u>
I	8.3	0.690
II	6.7	0.320
III	11.0	0.310
IV	3.9	0.230
V	4.3	0.190
VI	2.3	0.160

Table III contd.

Compound	<u>Net dispersion</u> <u>Vol. of auxiliary</u> <u>agent solution</u> <u>5 c.c. of 1%</u>	<u>Point light method</u> <u>% Concentration of cal-</u> <u>cium chloride solution</u>
VII	2.7	0.130
VIII	0.34	0.120
IX	12.3	0.321
X	6.6	0.276
XI	7.0	0.620
XII	5.5	0.290
XIII	6.6 (5 c.c. of 2% wetting agent was used)	0.115
XIV	6.1	0.310
XV	0.0	0.160
XVI	0.34	0.140
XVII	8.6	0.640
XVIII	10.0	0.680
XIX	4.9	0.260
XX	1.85	0.145
XXI	1.3	0.218
XXII	0.3	0.206
XXIII	2.4	0.157
XXIV	11.7	0.546
XXV	3.0	0.333 244
XXVI	2.7	0.194

Table III contd.

Compound	<u>Net dispersion</u>	<u>Point light method</u>
	<u>Vol. of auxiliary agent solution</u> <u>5 c.c. of 1%</u>	<u>% Concentration of calcium chloride solution</u>
XXVII	2.6	0.170
XXVIII	0.7	0.194
XXIX	1.0	0.230
XXX	6.7	0.145
XXXI	5.9	0.285
Product Y	12.5	0.319

The substances ranged in the following decreasing order of efficiency: Product Y, (IX), (XXIV), (III), (XVIII), (XVII), (I), (XI), (II), (XXX), (X), (XIII), (XIV), (XXXI), (XII), (XIX), (V), (IV), (XXV), (VII), (XXVII), (XXIII), (VI), (XX), (XXI), (XXIX), (XXVIII), (VIII), (XVI), (XXII), (XV).

In all the cases lauric acid compounds were found to be better than the corresponding oleic acid compounds. Except for lauryl-p-anisidide-2- and -3-sodium sulphonates (III) and (I) respectively where the m- compound was better than the o-compound in all the other derivatives of alkoxyaniline; sulphonic acids, the o-compounds were better than the m-compounds. In xylidide derivatives, however, the m-compound was found to be superior to the o-derivative. In o-toluidides, m-orientation gave better products than p-orientation.

C-Alkoxy and C-alkyl substitution in the benzene ring in lauryl and oleyl metanilides and orthanilides gave compounds less resistant to hard water. C-Methoxy substituted compounds were more resistant to hard water than the corresponding C-ethoxy derivatives.

The calcium soap dispersing power went on decreasing, as the length of the fatty acid chain in lauryl-p-toluidide -2-sodium sulphonate went on increasing. Amongst the derivatives sulphonic acid, the product from mowhra oil fatty acids had the best calcium soap dispersing power, and the condensate from coconut oil fatty acids was second in order.

(ii) Point light method: To a 2.5-cm. diameter Nessler tube, 10 c.c. of N/50 sodium oleate solution, 2 c.c. of 1% auxiliary agent solution and 8 c.c. of calcium ^{chloride} solution of varied concentrations were successively added, the mixture stirred quickly with a glass rod and after one minute the point light (produced by inverting a tin having a pin point at the bottom over a 25 watt electric bulb) observed vertically downwards through the column of liquid. The strengths of calcium chloride solution which rendered the light just invisible are recorded in Table III. The determination was carried out in a dark room and a change of 0.005% in the strength of the calcium chloride solution gave a marked variation in the duration in which the point light could be

observed. The earlier view (Ramachandran, Uppal and Venkataraman, loc. cit.) that the titration method was the better method could not be confirmed. In the point light method, the results could be duplicated easily and the method was more quick. In the titration method in some cases it took hours to filter and wash the precipitated calcium oleate. Again the uniformity of the filter bed of asbestos on glass wool in different determinations could not be duplicated and has to be assumed. The N-point of the change from green to grey was in many cases not marked.

The compounds were in the following order according to the decreasing order of efficiency: (I), (XVIII), (XVII), (XI), (XXIV), (IX), (II), Product Y, (III), (XIV), (XII), (XXXI), (X), (XIX), (XXV), (IV), (XXIX), (XXI), (XXII), (XXVI, XXVIII), (V), (XXVII), (VI, XV), (XXIII), (XX, XXX), (XVI), (VII), (VIII).

The values obtained were not in the same order as dispersion power obtained by the titration method, although compounds having good dispersing power gave high values by either methods, while the poorer products gave divergent values by the two methods. The lauric acid compounds again showed superiority over the oleic acid compounds. All the C-methoxy compounds were better than the C-ethoxy derivatives. In the alkoxy anilines the o-compounds showed higher calcium

soap dispersion power than the m-compounds, while in xylylidine derivatives the reverse was found to be the case. In o-toluidides, the m-compound again was superior to the p-compound. Introduction of one C-alkyl group did not change the dispersion power substantially, but with two C-alkyl groups as in xylylides the calcium soap dispersing power increased as shown by the point light method. A further increase in C-alkyl group as in cumidides decreased the dispersing power. Introduction of C-alkoxy group decreased the dispersion power in orthanilic and metanilic acid compounds.

Congo Rubine number: (Cf. Baudouin, Melliand Textilber., 1936, 17, 654, 932). Congo Rubine was purified by repeated precipitation of a hot saturated aqueous solution with potassium acetate and removal of the latter with boiling absolute alcohol (Neale, J. Soc. Dyers Col., 1936, 52, 252).

Congo Rubine solution (0.05%, 2 c.c.) was mixed with varying volumes of solutions of auxiliary agents in a test tube the whole made up to 15 c.c. by the addition of distilled water and mixed with 5 c.c. of 10% sodium chloride (Merck's extra pure quality). The colour change from red to lilac was observed after 10 minutes and the amount of auxiliary agent in mg. just sufficient to prevent the change noted (Table IV).

Table IV

<u>Compound</u>	<u>Amount of auxiliary agent in mg.</u>
I	35
II	Even 130 mg. not sufficient
III	32
IV	Even 130 mg. insufficient
V	30
VI	36
VII	Wetting agent salted out and the colour change could not marked.
VIII	80
IX	8.75
X	30
XI	37
XII	110
XIII	6.25
XIV	Even 130 mg. insufficient
XV	" "
XVI	120
XVII	6.0
XVIII	6.0
XIX	130
XX	60.5
XXI	47.5

Table IV contd.

<u>Compound</u>	<u>Amount of auxiliary agent in mg.</u>
XXII	27.5
XXIII	75.4
XXIV	3.5
XXV	30.1
XXVI	50.0
XXVII	8.0
XXVIII	85.0
XXIX	50.0
XXX	40.0
XXXI	45.0
Product Y	12.5

Compound (XXIV), lauryl-m-4-xylylidide-6-sodium sulphonate was found to be the best, and (XVII), (XXVII) and (XVIII) were found to have higher protective colloidal action than Igepon T (Product Y). In the majority of cases lauric acid compounds were better than oleic acid compounds. No definite conclusion could be drawn about the influence of the position of the sulphonic group and the protective colloidal action. While in C-alkoxyanilines the o-compounds were generally superior to the m-compounds, in m-4-xylylidides the reverse was found to be the case.

C-Ethoxyanilides were found to be superior to the corresponding C-methoxy compounds, but introduction of the C-alkoxy

group in the benzene ring did not give better protective colloids. In the lauric acid derivatives of metanilic and orthanilic acid, introduction of C-alkyl groups gave superior products, but in the oleic acid derivatives the resulting compounds were less efficient than the original products. As the number of C-alkyl groups in C-alkyl laurylanilide-m-sodium sulphonate was increased the protective colloidal action increased up to two C-alkyl groups, but diminished with a further increase, as in the cumidine derivative, but in the corresponding orthanilides the toluidide compound was found to be the best, the xylidine compound (XXVII) being less efficient.

In the saturated fatty acid derivatives of p-toluidine-2-sulphonic acid, the protective action diminished with the increase in the fatty acid chain. The compound from mixed fatty acids from mowhra oil had very good protective colloidal action.

Aqueous method for preparing carboxyamides.

In addition to the standard procedure for the condensation of acid chlorides and arylamine sulphonic acids in pyridine solution, it has been found feasible to effect the condensation in acetone and in aqueous solution in the presence of alkalies like sodium carbonate and caustic soda.

The general method followed was similar to that described

in I. C. I. patent (B.P. 452,139) in which the condensation of p-phenetidine-2-sulphonic acid and oleyl chloride in aqueous alkaline solution was described. Experiments to condense different acid chlorides and amino sulphonic acids in aqueous and acetone solution were tried.

The preparation of lauryl-p-toluidide-2-sodium sulphonate by condensing lauryl chloride and p-toluidine-2-sulphonic acid in the presence of alkalies like caustic soda and sodium carbonate was studied as a typical example to arrive at an optimum and a general method for the preparation of carboxylamides.

(1) The aminosulphonic acid (2.5 g.) was dissolved in dilute sodium carbonate solution (100 c.c. of 1%) and excess of lauryl chloride (3.5 g.) was added gradually under stirring while the reaction was kept alkaline by additions of 2% sodium carbonate solution. The mixture was agitated for three hours and acidified with dilute sulphuric acid, and the unreacted lauric acid was extracted with ether, and the aqueous solution after neutralising with 10% caustic soda solution was taken down to dryness and purified by extraction with ethyl acetate. Both the residue (9 g.) and the purified product (0.2 g.) did not lather in aqueous solution.

(2) The above experiment was repeated using 0.5% caustic soda solution (100 c.c.) and using 1% alkali to keep the

reaction mixture alkaline. The residue after extraction with ethyl acetate (7 g.) and the extract (0.6 g.) had little lathering power.

(3) The aminosulphonic acid (2.5 g.) was converted into the sodium salt by exactly neutralising with caustic soda and taken down to dryness. The dry sodium salt (2.85 g.) was then condensed with equivalent quantity of lauryl chloride (2.9 g.) in the presence of dioxan (10 c.c.) and the contents refluxed for two hours on an oil bath at 110°C. After cooling the contents were filtered. The residue (2.9 g.) and substance obtained by evaporating the dioxan (2.7 g.) were again poor wetting agents.

(4) A mixture of the sulphonic acid (2.15 g.) and anhydrous sodium carbonate (2.1 g.) was suspended in acetone (100 c.c.) and equal quantity of lauryl chloride (2.5 g.) was added and the mixture refluxed on water bath for three hours. The solvent was evaporated off and the residue (6.3 g.) obtained gave a clear solution in water which lathered powerfully. A 0.1% solution gave a sinking time of 15 seconds, and 0.05% solution 55 seconds.

(5) The above experiment was repeated using sodium acetate (2 g.) in place of sodium carbonate. The crude product (5.2 g.) obtained, however, had little lathering property.

(6) Here carbon tetrachloride was used in place of acetone, while other conditions were the same as in experiment No. (4). The crude wetting agent (6.3 g.) gave a sinking time of 19 seconds at 0.1% concentration and 93 seconds at 0.05% concentration.

(7) p-Toluidine-2-sulphonic acid (4 g.; 1 mol) was dissolved in caustic soda solution (4.3 c.c. of 20%)(1 mol) and the solution stirred in a test tube and cooled to 0-5°C. and lauryl chloride (4.7 g.; 1 mol) and a concentrated solution of alkali (4.3 c.c. of 20%; 1 mol) were run in gradually keeping the mixture alkaline throughout. The mixture was stirred at 0-5°C. for 3 hours and taken down to dryness. A cream coloured powder (9.0 g.) was obtained. The soap was determined by acidifying a 2% solution of the wetting agent with sulphuric acid, extracting with ether and titrating the ether extracted matter with alkali. The unreacted amine was found by titrating with standard sodium nitrate solution. The sample prepared contained 21.7% of free sodium laurate and 4.3% of unreacted p-toluidine-2-sodium sulphonate.

(8) In experiment No. 7 the final reaction mixture was extremely viscous and could not be worked properly. The high percentage of soap formed may be due to inefficient mixing of the reaction mixture. The conditions were therefore modified by using more dilute alkali \dot{a} in the beginning (8.6 c.c. of 10% caustic soda), while the other factors remained the same.

The final product was a gritty cream coloured powder (9.25 g.). On examining it was found to contain 17.1% of the free soap and 7.7% of the unreacted sodium salt of the amino sulphonic acid.

(9) In this experiment all the alkali required in the reaction is taken in the beginning in the form of a 10% solution (17.2 c.c.), the other conditions remaining the same as in (7). The crude product (9.2 g.) contained 9.5% of the free soap and 2.3% of unreacted p-toluidine-2-sodium sulphonate. The wetting power and the calcium soap dispersion of the product were determined.

As will be observed from the different experiments a certain amount of soap and unreacted sodium salt of the arylamine sulphonic acid were always left in the reaction. To note the precise influence of these adulterants on the wetting power and calcium soap dispersion, pure lauryl-p-toluidide-2-sodium sulphonate obtained by the extraction of the crude with ethyl acetate was adulterated with different quantities of the soap on the one hand, and p-toluidine-2-sodium sulphonate on the other, to give a mixtures which correspond more or less with the final reaction products obtained in experiments 8, 9 and 10. Solutions of the pure wetting agent and sodium laurate in such proportions that the final solution contained the wetting agent to sodium laurate

in the proportions of 70:30; 80:20 and 90:10 were made (Mixtures I, II, III respectively). Similarly the wetting agent solution was mixed with a solution of p-toluidine-2-sodium sulphonate to give mixtures IV and V in which the proportion of the wetting agent to the aminosodium sulphonate was 90:10 and 98:2 respectively. The wetting power for these mixtures, as well as for the crude wetting agent (mentioned as Product A), pure lauryl-p-toluidide-2-sodium sulphonate, commercial and pure Igepon T was determined by the Herbig number and the flotation methods and their resistance to hard water was determined by the titration method. The results are tabulated in Table V.

Table V/

Table V

Wetting agent	Herbig number		Draves test		Calcium soap dispersion Net dispersion C.c. of 0.1N HCl	
	% Concentration		% Concentration			
	0.25	0.1	0.1	0.05		
Mixture I	69.4	61.8	55.3	10.0	14	6.35
" II	70.0	62.0	54.8	7.8	15	7.55
" III	68.7	63.0	58.3	6.5	18	11.7
" IV	69.2	61.7	54.1	8.0	15	12.2
" V	69.7	62.7	56.0	7.0	18	12.25
Product A	66.5	60.9	54.8	11.0	24	10.1
Lauryl-p-toluidide- 2-sodium sulpho- nate (Compound IX)	67.6	61.7	58.4	6.0	20	12.3
Commercial Igepon T	56.0	49.2	35.6	45-60	Above 3 mins.	2.1-2.9
Pure Igepon T	58.5	54.7	52.0	20.0	42	12.5

It was observed that admixture of the wetting agent with soap gave higher wetting power, but reduced resistance to hard water, due to instability of the soap to hard water. Wetting agent containing about 10% soap was, however, quite as efficient as pure compound itself, the precipitated calcium soap apparently being dispersed by the wetting agent present. The presence of p-toluidine-2-sodium sulphonate even when it was 10% of the total mixture did not adversely affect the wetting power of the calcium soap dispersing power of the wetting agent.

It was concluded that the method outlined in experiment (10) may be taken as optimum as the amount of soap and unreacted p-toluidine-2-sodium sulphonate in the final reaction mixture does not interfere with its utility as a wetting agent.

Determination of interfacial tension.

A 5-c.c. Gardner and Holdt Surface Tension Meter was used. The apparatus is used for measurement of interfacial tension of two immiscible liquids.

The number of drops formed by a definite volume of liquid is inversely proportional to the interfacial tension. The temperature, the depth of immersion of the capillary tip was kept constant and the beaker was always filled to the same height and the instrument rested on the bottom.

The apparatus was filled to the mark with kerosene oil and fixed exactly vertical with the lower end dipping in

80 c.c. of 0.05 to 2.0% solutions of Igepon T, Nekal BX and sodium laurate in a 100 c.c. beaker. The rate at which the drops issued from the tip was regulated so as not to allow too rapid a formation of drops. The rate of drops was kept nearly constant at 120-130 seconds for 100 drops throughout the different determinations by controlling the air-inlet. The number of drops in allowing 5 c.c. of the kerosene to flow out was noted. The greater the number of drops greater the wetting power.

Commercial Igepon T and Nekal BX were purified by extracting with hot redistilled dioxan dried in vacuo before use. Lauric acid (Dr. Theodore Schuchardt's) was accurately weighed and melted in hot distilled water, and titrated with 0.1N caustic soda solution and finally made up to 500 c.c. to give a 2% solution. Freshly distilled water was used in each experiment. The hydrogen ion concentration of water used was 4.8 and the determinations were made at room temperature (29°C.). The drop numbers and their reciprocals at different concentrations of the three wetting agents are given in Table VI and graphically represented in Fig. VII.

Table VI/

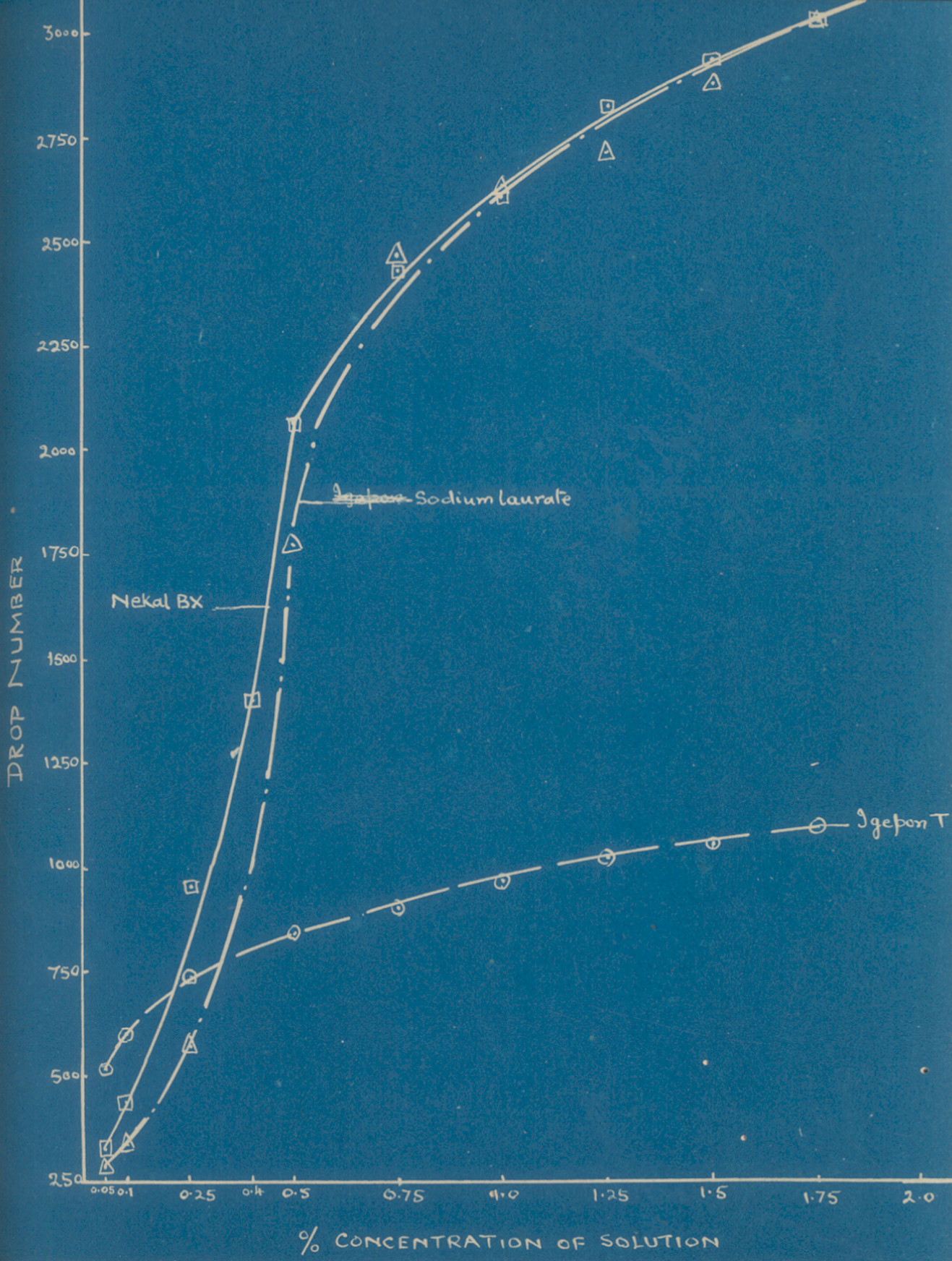


Table VI

Concen- tration %	Nekal BX		Igepon T		Sodium laurate		
	Drop No.	Drop rate in secs. $\frac{-40}{x10}$	Drop No.	Drop rate in secs. $\frac{-4}{x10}$	Drop No.	Drop rate in secs. $\frac{-4}{x10}$	
0.05	330	127	517	130	279	124	35.84
0.1	438	126	604	123	341	129	29.33
0.25	962	129	743	129	574	121	17.42
0.4	1407	121	7.125				
0.5	2070	122	4.8	120	1775	122	5.634
0.75	2435	120	4.103	125	2477	120	4.037
1.0	2620	125	3.817	121	2644	120	3.782
1.25	2835	119	3.528	124	2730	119	3.663
1.5	2953	119	3.387	132	2891	118	3.459
1.75	3050	124	3.279	124	3042	122	3.287
2.0	3145	119	3.180		3140	118	3.185

It was seen that in case of Nekal BX and sodium laurate there was a very sharp increase in the number of drops as the concentration of the solution was increased but above 0.5% the increase in drop number was much more gradual. The increase in drop number in Igepon T was, however, more gradual.

To find the relation between the drop number and the rate of drops, drop numbers of solutions of Nekal BX at 0.25 0.4 and 0.5% concentrations were determined at different rates of drops. The results are given in Table VII and show that by increasing the rate of issue of drops, the drop number was reduced, and the change was more marked in concentrated solutions.

Table VII

Drop numbers of Nekal BX at different drop rates.

<u>0.25% Conc.</u>		<u>0.4% Conc.</u>		<u>0.5% Conc.</u>	
Average time time in Drop No. secs. for 100 drops		Average Drop time in No. secs. for 100 drops		Average Drop No. time in secs. for 100 drops	
54.5	891	102	1128	125	2084
112.5	946	110	1350	215	2270
142.1	978	246	1525		
229.0	979				

Dispersibility of calcium soaps of saturated fatty acids.

The fatty acids were accurately weighed (Dr. Theodore Schuchardt's products) and dissolved in neutral alcohol and titrated with 0.1 N caustic soda solution using phenolphthalein as indicator. The alcohol was evaporated off on a steam bath and the soap was dissolved in distilled water and made up to 100 c.c. Requisite amount of this stock solution was taken and made to 100 c.c., so as to get 0.02 N solution of the soap. A 0.111% or 0.02 N solution of calcium chloride was made by diluting 111 c.c. of 1% calcium chloride solution to a litre.

Titration method:

Experiment (I): The soap solution (10 c.c. of 0.02 N) was diluted with distilled water (25 c.c.) in a stoppered conical flask. The calcium chloride solution (10 c.c. of 0.02 N) was added, and the mixture was vigorously shaken and filtered through a bed of Gooch asbestos spread on glass wool after 5 minutes. The precipitated soap was washed thrice with 10 c.c. portions of distilled water. The dispersed soap was titrated with 0.1 N hydrochloric acid using Linstead's mixed indicator to a neutral grey point.

Experiment (II): In the above experiment the sodium palmitate and stearate which were in the form of jellies in

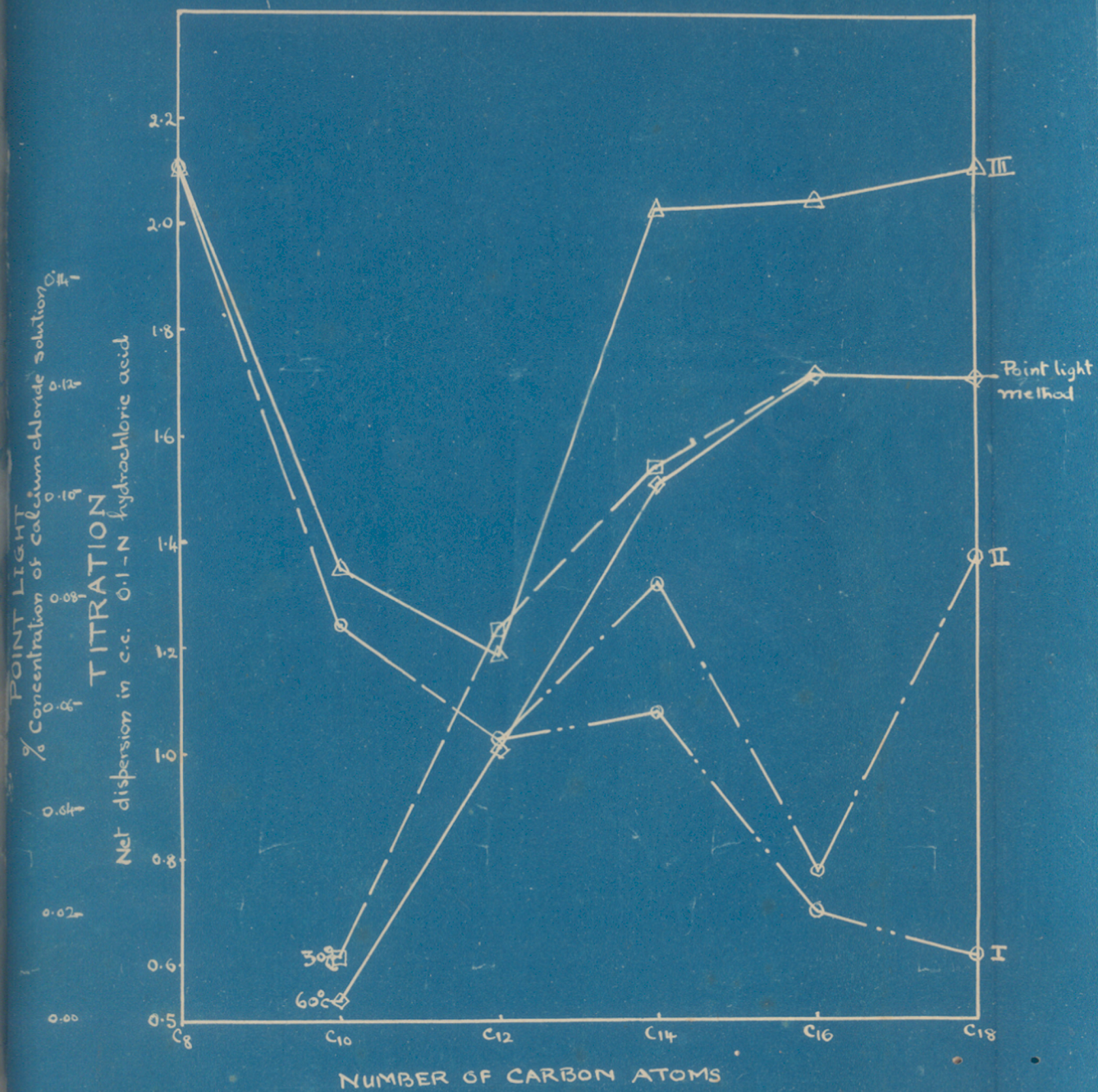


Fig. VIII

Solubility of calcium soaps of saturated fatty acids

cold and sodium myristate as a turbid solution were used measured out as such. In the next experiment the clear soap solutions (10 c.c.) were ~~pre~~pped out in hot, and diluted in water (25 c.c.). After cooling the soap solution to 30°C., the calcium chloride solution was added and the test carried out as usual.

Experiment (III): The third experiment, the calcium soap dispersion was determined at 60°C., using hot soap and calcium chloride solutions. Results of these experiments are given in Table VIII and graphically represented in Fig. VIII.

Table VIII

<u>Soap</u>	<u>Net dispersion</u>			<u>Point light method</u>	
	<u>Experiment No.</u>			<u>% Concentration of</u>	
	<u>I</u>	<u>II</u>	<u>III</u>	<u>calcium chloride</u>	<u>calcium chloride</u>
				<u>30°C.</u>	<u>60°C.</u>
Sod. caprylate C ₈	2.11	2.11	2.11	-	-
" caprate C ₁₀	1.24	1.24	1.35	0.0136	0.0085
" laurate C ₁₂	1.03	1.03	1.19	0.07575	0.0527
" myristate C ₁₄	1.08	1.32	2.03	0.1088	0.102
" palmitate C ₁₆	0.70	0.78	2.05	-	0.124
" stearate C ₁₈	0.62	1.38	2.11	-	0.122

The soaps may be arranged according to the decreasing dispersion as follows:

Experiment I:- C₈, C₁₀, C₁₄, C₁₂, C₁₆, C₁₈

Experiment II:- C₈, C₁₈, C₁₄, C₁₀, C₁₂, C₁₆

Experiment III:- C₈, C₁₈, C₁₆, C₁₄, C₁₀, C₁₂.

Calcium caprylate therefore was completely dispersed in hot and cold and calcium stearate in hot was also dispersed completely. The dispersion at 60°C. decreased with the increase in carbon atoms in the acyl chain up to C₁₂, and then sharply increased, calcium myristate, palmitate and stearate being almost completely dispersed. In cold (30°C.) the dispersion slightly increased from C₁₂ to C₁₄, but again there was a gradual decrease afterwards, although the decrease again was irregular after C₁₂ when the test soap solutions were taken hot, diluted and used.

The soaps of caprylic, myristic and palmitic and stearic acids can therefore be employed in hard water at temperatures above 60°C. As against the dispersive power for calcium oleate, in which sodium laurate is best, the dispersibility of the calcium laurate itself is very low, and while the dispersion power of sodium caprylate is low, the dispersibility of the calcium caprylate is highest.

Point light method: The soap (10 c.c., 0.02N) and a solution of calcium chloride of varying concentrations were

mixed in a Nessler tube and the point light observed. The critical concentration of calcium chloride required to just observe the point light after one minute was determined. The determination was made in cold (29°C.) and in hot (60°C.), as sodium stearate and palmitates were insoluble in cold. As no caprate was left for the experiment, the tests were done for higher soaps. The solubility increased with increased length of the alkyl chain, and calcium soaps of stearate and palmitate were completely dispersed at 60°C. By this method the laurate was dispersed more than the caprate. Another observation contradictory to titration method was the decreased solubility of the calcium soaps at higher temperatures.

Preparation of pure lauric acid.

Cocconut oil (100 g.) was saponified with 10% caustic soda and decomposed with dilute sulphuric acid. The fatty acids liberated were extracted with ether and washed free from mineral acid. After drying over unhydrous sodium sulphate the ether extract was distilled and the residue of the mixed fatty acids was dried at 100-105°C. (Yield 87 g.), and used for fractionation.

Vacuum distillation of the mixed fatty acids: The mixed fatty acids (63.5 g.) were taken in a vigreux flask and connected to Cenco vacuum pump through a distillation triangle

and a manometer tube. A few pieces of porcelain were added for uniform boiling. The flask was gradually heated in an oil bath up to 210°C., and directly heated afterwards to collect higher fractions. When the distillation had started, the bath temperature was kept constant till all the fraction had come over. When the fraction had distilled over the temperature of the distillate fell down, and to collect the higher fractions the bath temperature was further raised. Seven distinct fractions were collected in separated flasks and weighed. A sample of each fraction was dissolved in neutral alcohol and titrated with standard alkali to determine the mean molecular weight. The melting point of the fractions were also determined. The results of the fractionation are given in Table IX.

Table IX/

Table IX

Fraction No.	Temperature range for distillation on °C.	Bath Temperature °C.	Pressure mm.	Yield g.	Melting point °C	Acid taken for titre g.	0.07657N caustic soda required c.c.	Mean molecular weight	Mean
1	100-103	175	3	3.5	0.1804	16.1	146.3	145.6	
2	115-119	187	4	4.2	0.2738	24.7	144.8	158.8	
3	130-135	200	2.6	3.15	0.2236	18.6	157.5	186.9	
4	140-145	210	2.6	26.3	0.1860	13.0	186.8	204.1	
5	145-146	Direct heating	1.8	9.0	0.2060	14.4	187.0	225.7	
6	155-158	"	1.8	6.4	0.1190	7.6	205.0	237.7	
7	165-173	"	1.8	2.6	0.1630	10.4	203.2	250.6	
					0.1480	8.6	225.0		
					0.2114	12.2	226.3		
					0.1920	10.6	237.7		
					0.2084	11.5	237.7		
					0.3554	18.5	250.8		
					0.3210	16.8	250.3		

Lauric acid marketed by Dr. Theodore Schuchardt melts at 42.5°C . and gave a mean molecular weight of 205.4. Number 4 fraction which corresponds nearly to pure lauric acid forms 41.8% of the total fatty acids taken for distillation. A total distillate of 55.05 g. was collected, indicating a loss of 8.45 g. in the distillation process, mostly as residue left in the flask, the acid sticking to the distilling ends and the distillation triangle.

Myristic acid from nutmeg seeds.

The shells (1 lb.) were broken open and the kernels (299 g.) were powdered and extracted in a soxhlet with 95% alcohol. The alcoholic extract on cooling to 5°C . gave clusters of the fat which melted at $54-55^{\circ}\text{C}$., corresponding to trimyristin (47.5 g.). The fat was saponified and the soap decomposed with dilute sulphuric acid when myristic acid was obtained as a yellow brown solid (40.1 g.), melting at $51-52^{\circ}\text{C}$., which corresponds to Schuchardt's product which melted at $52-53^{\circ}\text{C}$.

Sulphonation of aniline by sulphamic acid.

Freshly distilled aniline (28.8 g., 2 mols) and sulphamic acid ~~were~~ (15 g., 1 mol) were heated together in a 100-c.c. ground glass necked round bottomed flask fitted with an air condenser and a calcium chloride tube in an oil bath at $200-210^{\circ}\text{C}$. for one hour. The bluish violet reaction mixture

was then poured out in a mortar and allowed to cool. It solidified on cooling and formed a sticky grey mass. It was pacted with ether when a grey powder was obtained. The ether extract was filtered off and the residue shaken thrice with 50 c.c. portions of ether in a separating funnel and filtered. The filtrate was distilled to remove the ether and the unreacted aniline was removed (8.6 g.). The residue after ether extraction was suspended in water (200 c.c.) heated in a dish on steam bath. A solution of barium hydroxide (50 g. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in 300 c.c. water) was added and the heating continued till all the ammonia was driven off. The contents were then acidified with a slight excess of dilute sulphuric acid (9 c.c. of concentrated sulphuric acid were diluted in 50 c.c. water and used). After heating for 10 minutes the contents of the dish were filtered hot, and the residue extracted thrice with 150 c.c. portions of boiling water. The total filtrates were then concentrated to 300 c.c. and cooled in ice, when elongated colourless plates (parallelograms and in some cases hexagons) separated. These were collected and dried at 105°C . when a pink coloured powder (4.45 g.) of the sulphonic acid was obtained. By concentrating the filtrate after separation of the first crop of crystals to 50 c.c. and cooling a second crop of crystals was obtained (3.6 g.).

Identification of the sulphonic acid: A portion of the sulphonation product after recrystallising from water gave a

pure product which contained sulphur and absorbed alkali when titrated with 0.1 N caustic soda solution. The purity of the sulphonic acid, however, could not be determined by titrating with alkali, as the end point was not sharp. On adding excess alkali the reaction product went in solution, thereby showing that it must be a sulphonic acid from aniline and not aniline sulphate, as the latter would have given drops of aniline on treating with alkali. To identify the sulphonic acid the p-toluenesulphonyl derivative and its p-chloraniline salt were prepared.

p-Toluenesulphonyl derivative:- The recrystallised dry sulphonic acid (1.73 g., 1 mol) and p-toluenesulphonyl chloride (1.9 g.) were heated together with dry distilled pyridine (10 c.c.) in a round bottomed flask fitted with an air condenser and a calcium chloride tube, in an oil bath at 140-150°C. for three hours. The mixture became very warm and deep orange in colour initially and at the end of the reaction, a precipitate was obtained. It was filtered and washed with distilled water (20 c.c.). The residue was crystallised from boiling water after decolourising with norit charcoal, when elongated plates separated. The pure derivative melted at 265°C. and compares with the p-toluenesulphonylsulphanilic acid prepared earlier.

p-Chloraniline salt of p-toluenesulphonylaniline-

sulphonic acid:- A portion of the p-toluenesulphonyl derivative was boiled with water and made alkaline to phenolphthalein with a solution of 10% caustic soda, and boiled to remove pyridine. A slight excess of acid solution of p-chloraniline hydrochloride was then added and boiling continued for 10 minutes. On cooling the p-chloraniline salt separated. It was recrystallised from boiling water after noriting, when the derivative was obtained as elongated plates or flat needles. It melted at 236°C. and compared with the p-chloraniline salt of p-toluenesulphonylsulphanilic acid prepared earlier which also melted at 236°C. The mixed melting point of both the products was the same. The product on analysis gave S, 13.95. $C_{19}H_{20}O_5N_2S_2$ requires S, 14.1%.

It was therefore concluded that sulphonating aniline by sulphamic acid under conditions described, the sulphonic acid group entered into the para position to the amino group giving sulphamic acid.

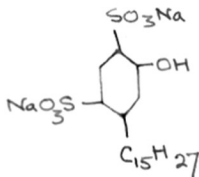
Derivatives of cashew nut shell oil.

Preparation of anacardol: Powdered cashew nut shells were extracted in a soxhlet with benzene, and the oil was obtained by distilling off the solvent. It was distilled in a Claissen's flask under vacuum. The oil (100 g.) on distillation at 240-260°C./10 mm. gave 65 g. of anacardol as a yellow oil. Considerable frothing occurred during the early

stages of the distillation, but ~~was~~ when the frothing had ceased the liquid distilled smoothly. Anacardol thus obtained became light brown after some days. It was directly used in the synthetic experiment without further purification.

Preparation of tetrahydroanacardol: Anacardol (5 g.) was dissolved in 95% alcohol (50 c.c.) and hydrogenated in the presence of Adam's platinum oxide catalyst in a Parr hydrogenation apparatus, at 40-45 lb. pressure and at room temperature for 2 hours, when the hydrogenation was completed. The mixture was filtered after decantation of the suspended catalyst. On distilling off from the solvent a light brown oil was left which set to a brownish solid on cooling. The tetrahydroanacardol could be crystallised from petroleum ether (60-70°C.), but in the present work the crude product itself was used.

Sulphonation of anacardol.

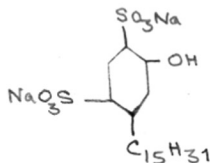


Anacardoldisodium sulphonate (I)

A mixture of 80% fuming sulphuric acid (3.5 c.c.) and trichlorethylene (2.5 c.c.) was stirred in a 100 c.c. round bottomed flask, fitted with a mechanical agitator and externally

cooled in a freezing mixture. A solution of anacardol (5 g.) in trichlorethylene (5 c.c.) after cooling to 0°C. was gradually added to the flask under stirring and the mixture worked at 0°C. for 1 1/2 hours, when the sulphonation mixture became water soluble. The deep brown paste obtained was diluted with crushed ice and the aqueous solution neutralised to phenolphthalein with 10% aqueous solution of caustic soda and taken down to dryness on a water bath. The residue was powdered and extracted with absolute methyl alcohol in cold. The extract after leaving overnight was filtered off to remove some white sediment which separated, and the filtrate was distilled to remove the solvent and the residue was dried in oven at 100°C. The product was olive brown light powder, which was extremely hygroscopic (yield 4.8 g.). On analysis it was found to be a disodium salt of anacardoldisulphonic acid (found S, 12.8; Na, 9.3. $C_{21}H_{30}O_7S_2Na_2$ requires Na, 9.1%; S, 12.6%.

Sulphonation of tetrahydroanacardol:

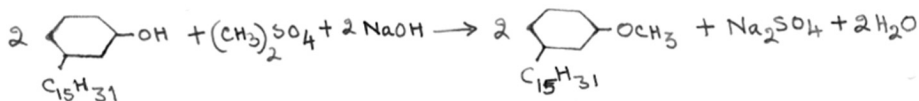


Tetrahydroanacardol disodium sulphonate(II)

Tetrahydroanacardol (5 g.) was added gradually to 20% fuming sulphuric acid (12.5 c.c.) kept stirred up in a 100 c.c. round bottomed flask, externally cooled with crushed ice. The mixture was stirred at 0°C. for 2 hours and finally at 50°C. for one hour and then dissolved in ice water. The solution was neutralised to phenolphthalein with 10% caustic soda solution and concentrated to 150 c.c. and left in the refrigerator overnight. A white mass of crystals separated, which was collected dried and finally purified by extracting with methyl alcohol. After removing the solvent the light gritty powder was dried at 100-105°C. (Yield 6.2 g.) . On analysis it was found to be the disodium salt of tetrahydroanacardol disulphonic acid (Found: Na, 9.2; S, 12.4. $C_{21}H_{34}O_7S_2Na_2$ requires Na, 9.3%; S, 12.5%).

Preparation of o-methylether of anacardol: Anacardol (10 g.) was treated with dimethyl sulphate (21 g.) under alkaline following conditions as in the 1/11 experiment. The o-methylether of anacardol obtained (7.8 g.) was a deep yellow oil (Compound III).

Preparation of o-methylether of tetrahydroanacardol:



o-Methylether of tetrahydroanacardol (IV)

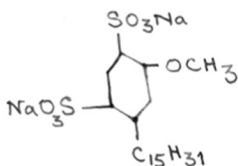
Tetrahydroanacardol (10 g.) (1 mol) was dissolved in acetone (40 c.c.) in an evaporating dish. The solution was then made alkaline to phenolphthalein with 10% caustic soda solution. Dimethyl sulphate (20.8 g., 5 mols) was then added gradually with stirring, keeping the mixture alkaline to litmus by additions of 50% caustic soda solution. The acetone was then distilled off and the reaction mixture was heated on water bath for an hour. After cooling the methylether of tetrahydroanacardol which separated as an oil was extracted with ether.. The ether layer was washed free from alkali and dried over anhydrous sodium sulphate. The ether was then distilled off when a yellow oil was obtained (8 g.).

The methylether was purified by distilling under vacuum. It distilled as a colourless oil at 215-230^o C. at 3 mm. pressure, which changed to pale yellow on keeping (6.5 g.).

Sulphonation of o-methylether of anacardol: The methylether (6 g.) was dissolved in trichlorethylene (6 c.c.) and after cooling to 0-5^o C. it was gradually added under stirring to a mixture of 20% fuming sulphuric acid (10 c.c.) and trichlorethylene (5 c.c.), cooled externally in crushed ice. The mixture was worked below 10^o C. for 2 hours, when it became water-soluble. The dark brown reaction mixture was dissolved in ice-cold water and neutralised with 10% caustic soda solution

and taken down to dryness. The crude dry product was purified by extracted with ethyl acetate, when the disodium salt of o-methylether of anacardol^(V) was obtained as a brownish powder (Found: Na, 8.9; S, 12.4. $C_{22}H_{32}O_7S_2Na_2$ requires Na, 8.8%; S, 12.3%):

Sulphonation of methylether of tetrahydroanacardol:

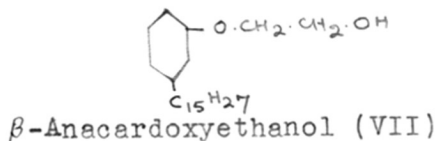


o-Methylether of tetrahydroanacardol disodium sulphonate
(VI)

The methylether of tetrahydroanacardol (6 g.) was kept stirred up in a test tube externally cooled with crushed ice. 20% fuming sulphuric acid (6.8 c.c.) was added gradually and the mixture stirred at 5-10°C. for 30 minutes and then at room temperature for one hour. For better working of the sulphonation mixture which had partially solidified, 5 c.c. of concentrated sulphuric acid was added and worked for 30 minutes, when a test portion gave a clear solution in water. The brownish paste was dissolved in cold water (5-10°C), after neutralising to phenolphthalein with 10% caustic soda, it was taken down to dryness on a water bath. The sulphonate was powdered and extracted with ethyl acetate. On distilling the solvent a solid gave the unreacted anacardol which was recovered by

cream coloured product was obtained (7.9 g.) (Found: Na, 8.6; S, 12.2. $C_{22}H_{36}O_7S_2Na_2$ requires Na, 8.8%; S, 12.3%).

Preparation of β -phenoxyethyl alcohol from anacardol:



Anacardol (15 g., 1 mol.) was dissolved in hot alcohol (10 c.c.) in a 250 c.c. 3-necked round bottomed flask fitted with a reflux condenser, and 10% caustic soda solution (80 c.c., 4 mols) were added. The contents were heated on boiling water bath and ethylene chlorhydrin (16 g., 4 mols) was gradually added through a separating funnel, with thorough shaking. The reaction mixture froths considerably during the addition of ethylene chlorhydrin. It was heated on water bath for three hours. On cooling a dark red oil was obtained as an upper layer. The lower aqueous layer was siphoned off and the oil extracted with ether and washed four times with 50 c.c. portions of 5% caustic soda solution. The ethereal layer was washed free from the alkali and the washings collected. The ether extract was dried over unhydrous sodium sulphate and filtered. On distilling the solvent, a dark brown oil was obtained (15.1 g.) The aqueous washings on acidification with dilute hydrochloric acid gave the unreacted anacardol which was recovered by

ether extraction (0.15 g. were recovered).

Identification of the β -phenoxyalcohol from anacardol:

The brownish oil obtained did not solidify even when cooled to 0°C. On heating in vacuum (10 mm. pressure) considerable frothing occurred, while ^{when} it was heated in partial vacuum (245 mm) the substance did not distil even up to 354°C., after which a dark yellow oil together with whitish fumes was obtained. It smelt like cashew nut shell oil (Found: C, 53.4; H, 9.1. $C_{23}H_{36}O_2$ requires, C, 80.2%; H, 10.4%), and partial decomposition appears to have taken place. On analysing the oil without distilling the following results were obtained: C, 78.7; H, 10.45; the required values being 80.2% and 10.4% respectively.

Derivatives of β -anacardoxyethyl alcohol:
(XIII)

3:5-Dinitrobenzoate: The alcohol (1 g.) was heated on water bath with 3:5-dinitrobenzoyl chloride (2.5 g.) in a dry test tube with a calcium chloride tube. The products reacted vigorously with effervescence. The sticky olive brown product obtained was washed with 2% sodium carbonate solution and finally with water. It was readily soluble in benzene and sparingly soluble in alcohol and ether. The benzene extract on evaporation gave a sticky brown substance, which ~~did~~ ^{sharply} not melt.

(XIV)
 Δ -Naphthylurathane: The alcohol (2 g.) and Δ -naphthylisocyanate (2 c.c.) were heated together on water bath for 5

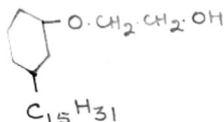
minutes in a dry test tube fitted with a calcium chloride tube. It was cooled in crushed ice, when the reaction mixture set to a solid which was subsequently boiled with petroleum ether (10 c.c.) and filtered hot. The filtrate does not give crystals even on keeping in freezing mixture for several hours. It was therefore taken down to dryness when a brownish viscous solid was obtained having no definite melting (Found: N, 3.0. $C_{34}H_{43}O_3N$ requires N, 2.7%).

(XV)

Toluene-p-sulphonyl derivative: The alcohol (1 g., 1 mol) and toluene-p-sulphonyl chloride (1.1 g. 2 mols) were heated together in the presence of pyridine (10 c.c.) for one hour at 140-150°C., in a round bottomed flask fitted with an air condenser. The deep brown reaction mixture was left overnight and poured on a mixture of crushed ice and dilute hydrochloric acid. A brown oil was obtained which ether extracted and washed free from acid. The ether layer after drying over anhydrous sodium sulphate was distilled when a dark brown liquid was left (Found S, 6.2. $C_{30}H_{42}O_4S$ requires S, 6.4%).

Another method of identification of β -anacardoxyethyl alcohol and β -tetrahydroanacardoxyethyl alcohol from the parent anacardol and tetrahydroanacardol was the inability of the former to give phenoxyacetic acid derivative with chloroacetic acid.

Preparation of β -phenoxyethyl alcohol from tetrahydro-
anacardol:



β -Tetrahydroanacardoxyethanol (VIII)

Tetrahydroanacardol (20 g., 1 mol) was dissolved in hot alcohol (20 c.c.) in a 250 c.c. 3-necked round bottomed flask fitted with a reflux condenser and 10% caustic soda solution (107 c.c., 4 mols) was added and the contents heated on a water bath. Ethylene chlorhydrin (21.8 g., i.e. 18 c.c., 4 mols) was added through a separating funnel drop by drop, the flask being shaken intermittently. There was considerable effervescence and the liquid frothed during the addition of ethylene chlorhydrin. After the addition the contents were further heated on water bath for four hours, and shaken frequently during the heating. On cooling to room temperature a yellow waxy solid separated which was extracted with ether in a separating funnel. The ether layer was washed twice with 100 c.c. of 5% caustic soda and finally with water till free from alkali. The ether extract was then dried over unhydrous sodium sulphate and filtered. The ether was distilled off, and

the residue dried in an oven at 105°C. On cooling a pale yellow coloured crisp solid was obtained, melting at 45-46°C. (Yield 20.3 g.). The condensation product was crystallised from petroleum ether (60-70°C.). The product easily dissolved in the solvent and separated as colourless plates from the saturated solution on cooling in a freezing mixture. The crystals, however, melt at room temperature and have therefore to be filtered off quickly from the solvent at low temperature on a Buchner flask connected to vacuum. On recrystallising the solid a product melting sharply at 48-48.2°C. was obtained as shining, lustrous plates.

Identification of β -tetrahydroanacardoxyethyl alcohol:

Determination of C and H in the compound: The compounds gave C, 80.1; H, 11.87. $C_{23}H_{40}O_2$ requires C, 79.3; H, 11.5%.


Preparation of derivatives of the β -phenoxyethyl alcohol of tetrahydroanacardol:

Preparation of 3:5-dinitrobenzoate: 3:5-Dinitrobenzoic acid (1.5 g.) was mixed with phosphorus pentachloride (1 g.) in a dry test tube fitted with a calcium chloride tube and the mixture was gently warmed to start the reaction. After initial rapid reaction had subsided the mixture was heated in a boiling water bath for 30 minutes and then poured in a watch glass, when it solidified to a brownish solid. The 3:5-dinitrobenzoyl

chloride was dried quickly by rubbing it on a porous tile with a spatula, to remove phosphorus oxychloride, and transferred to a clean dry sample bottle and stored in a desiccator (m.p. 75°C. given in literature Heilbraun 74°C.).

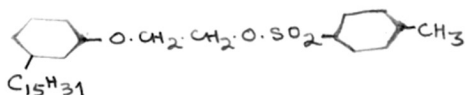
It was mixed with 0.5 g. of the β -tetrahydroanacardoxyethyl alcohol in a dry test tube fitted with a calcium chloride tube and heated in a boiling water bath for 30 minutes when considerable fumes were given out. After cooling, the reaction mass in the form of a plastic white solid was washed thrice with 10 c.c. portions of 2% sodium carbonate solution. It was then dried by rubbing it on porous tile and crystallised from hot ethyl alcohol (10 c.c.). β -Tetrahydroanacardoxyethyl-3:5-dinitrobenzoate_(XVI) was separated as a colourless needles by cooling the alcoholic solution in freezing mixture. These are collected dried on a porous tile and then in a vacuo over calcium chloride. The derivative melted at 63-63.5°C.. The alcoholic solution after separating the crystals was heated to boil and boiling water added till the solution was milky and then cooled in a freezing mixture when needles separated. These were collected as a light fluffy powder melting at 44.5-46°C. and was unreacted alcohol.

Preparation of α -naphthylurathane: β -Phenoxyethyl alcohol (0.5 g.) from tetrahydroanacardol was mixed with 0.5 c.c. of α -naphthylisocyanate (Eastman Kodak product) in a

dry test tube, fitted with a calcium chloride tube, and heated on a steam bath for 5 minutes. It was then cooled in a freezing mixture when the contents set to a light brown solid. Petroleum ether (60-70°C., 3 c.c.) was added and warmed to boiling point and the solution filtered hot. The filtrate was cooled in an ice bath and the urathane which separated as cream coloured mass was collected by pouring the ice-cold mixture quickly on a Buchner funnel. It was further crystallised from 3 c.c. of petroleum ether and finally from 2.5 c.c. of the solvent when the urathane^(XVII) separated as colourless needles melting sharply at 69-69.5°C. (Found: N, 2.9. $C_{10}H_7.NH.CO.OH_2.CH_2.O$  requires N, 2.7%).

Preparation of toluene-p-sulphonyl derivative

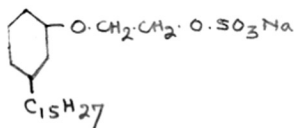
p-Toluenesulphonyl tetrahydroanacardoxyethanol (XVIII)



The phenoxy alcohol (1.5 g., 1 mol) and toluene-p-sulphonyl chloride (1.6 g., 2 mols) were mixed in a ground glass necked 100 c.c. round bottomed flask fitted with an air condenser and calcium chloride tube and 10 c.c. of pyridine (distilled over sodium) was added. The mixture became warm and orange in colour. It was heated at 120-130°C. from for

one hour and then left overnight. The brownish solution was poured over crushed ice (100 g.) and hydrochloric acid (5 c.c.). The reaction mixture was extracted with petroleum ether (90-100°C.), washed free from acid by shaking with water and dried over unhydrous sodium sulphate. After filtering, the solvent was distilled off when a brown oil was obtained. (Found: S, 6.1. $C_{30}H_{46}O_4S$ requires S, 6.4%).

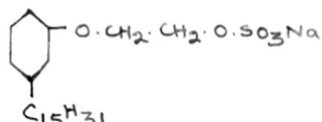
Sulphonation of β -anacardoxyethyl alcohol with chloro-sulphonic acid:



Sodium- β -anacardoxyethyl sulphate (.IX)

The β -anacardoxyethanol (3.5 g.) was dissolved in dioxan (3 c.c.), and the solution was added gradually to a mixture of chlorosulphonic acid (1.3 g.c.) and dioxan (2 c.c.) kept in a test tube fitted with an agitator and externally cooled in ice. The reaction mixture was worked at 0-5°C. for two hours. It was dissolved in cold water and after neutralising with 10% caustic soda solution it was taken down to dryness on a steam bath and purified with absolute alcohol. The extract was distilled off leaving a light brown sticky solid (3.7 g. Found: Na, 5.3. $C_{23}H_{35}O_5SNa$ requires Na, 5.2%).

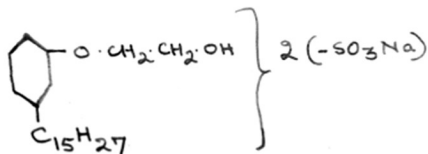
Sulphonation of β -tetrahydroanacardoxyethyl alcohol with chlorosulphonic acid:



Sodium- β -Tetrahydroanacardoxyethyl sulphate (XI).

A solution of the alcohol (3.5 g.) in dioxan (3 c.c.) was added gradually under stirring to a mixture of chlorosulphonic acid (1.4 c.c.) and dioxan (2 c.c.), kept in a test tube fitted with a mechanical agitator and externally cooled in ice. The mixture was worked below 10°C . for one hour when it gave a clear solution in water. It was dissolved in water, neutralised with 10% caustic soda solution and taken down to dryness on a water bath. The dry powder was extracted with absolute alcohol in cold. The extract after distilling the solvent gave a light brown product (3.5 g.) (Found Na, 5.3; S, 7.3. $\text{C}_{23}\text{H}_{39}\text{O}_5\text{SNa}$ requires Na, 5.1%; S, 7.1%) of the alcohol sulphate.

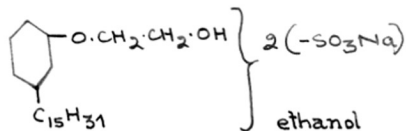
Sulphonation of β -anacardoxyethyl alcohol:



β -Anacardoxyethyl alcohol-disodium sulphonate (XI).

Fuming sulphuric acid (4.5 c.c. 60%) was added to dry distilled pyridine (1 c.c.) in a test tube fitted with an agitator and cooled externally with ice (0-5°C.). A solution of anacardoxy alcohol (4 g.) in pyridine (2.7 g.φ.) was added gradually to the test tube. The dark brown mixture was worked at 0-5°C. for two hours, when the reaction mixture gave a clear solution in water. It was diluted with crushed ice and neutralised with 10% caustic soda solution. It was taken down to dryness on a steam bath and finally dried in vacuum at 95°C. The brown powder obtained was extracted with cold absolute methyl alcohol. The pure product was brown hygroscopic powder (Found: Na, 8.6. $C_{23}H_{34}O_8S_2Na_2$ requires Na, 8.4%).

Sulphonation of β -tetrahydroanacardoxyethyl alcohol:



β -Tetrahydroanacardoxydisodium sulphonate (XII)

Fuming sulphuric acid (6.5 c.c. 60%) was added to sodium dry pyridine (1 c.c.) in a 100-c.c. round bottomed flask fitted with an agitator and cooled in crushed ice. A solution of the phenoxy alcohol (6 g.) in pyridine (4 c.c.) was added gradually to the flask under stirring. The mass was worked at 0-5°C. for 15 minutes and then at room temperature (28°C.) for 2 hours when the sulphonation mixture became water soluble.

The sulphonation mixture was dissolved in ice-cold water and neutralised to phenolphthalein with 10% caustic soda solution. The solution was then heated on steam bath to remove pyridine and finally taken down to dryness. The residue was powdered and extracted with 200 c.c. of hot methyl alcohol. The solvent extract was cooled to 10°C. and the inorganic impurities which separated were filtered off and after distilling the solvent the sulphonate was dried at 100-105°C. in the oven and finally over phosphorus pentoxide in vacuum. The light brown powder obtained was found to be a disodium salt of β -tetrahydroanacardoxyethyl alcohol disulphonate (Compound XII) (Found: Na, 8.5; S, 11.4. $C_{23}H_{38}O_8S_2Na_2$ requires Na, 8.3; S, 11.6%).

Derivatives of anacardol and tetrahydroanacardol: Both these products have been used as a starting materials for preparing wetting agents by direct sulphonation or by converting into the β -phenoxy alcohol and treating the latter. Different derivatives of phenoxyalcohols were prepared for identifying from the parent anacardol or tetrahydroanacardol. Derivatives were therefore prepared from anacardol and tetrahydroanacardol and compared with those obtained from the phenoxy alcohols.

Toluene-p-sulphonyl derivatives of anacardol and tetrahydroanacardol have been described earlier by Gandhi

(Ph.D. Thesis, Univ. Bombay). Both of these were liquids and do not serve to distinguish the phenoxy alcohols from the phenols.

3:5-Dinitrobenzoate of anacardol: A mixture of anacardol (1 g.) and 3:5-dinitrobenzoyl chloride (2.5 g.) was heated in water bath in a dry test tube fitted with a calcium chloride tube for 30 minutes. The reaction mixture was dark olive in colour and frothed considerably. It was treated with 2% sodium carbonate solution when a gummy sticky olive product was obtained. It was pasted with sodium carbonate solution several times and finally rubbed on a porous tile. The rubber like derivative was boiled with alcohol and filtered. On cooling the alcoholic extract needles of dinitrobenzoate separated, which were collected and dried. Some of the gummy substance (XIX) remained insoluble. The dinitrobenzoate/melted at 84-85°C.

Tetrahydroanacardol-3:5-dinitrobenzoate: Tetrahydroanacardol (1 g.) was treated with 3:5-dinitrobenzoyl chloride in a similar manner as anacardol. The deep brown reaction mixture on treating with dilute sodium carbonate solution gave effervescence with the formation of light brown sticky solid. After repeated washings with sodium carbonate it was finally washed with water when a light brown precipitate was obtained. It was dried over a tile and purified by crystallising from hot alcohol. The dinitrobenzoate/separated as needles melting (XX)

at 55-56^o C.

α-Naphthylurathane from anacardol: Anacardol (2 g.) and α-naphthylisocyanate (2 c.c.) were heated together in a dry test tube on boiling water bath for 5 minutes. After cooling the mixture was extracted with petroleum ether (6 c.c.) and the filtrate cooled in a refrigerator overnight when the urathane separated as a light brown product separated which was collected. The filtrate was evaporated to recover the dissolved urathane. The derivative^(XXI) is in the form of a viscous paste having^{no} definite melting point.

α-Naphthylurathane from tetrahydroanacardol: Tetrahydroanacardol (2 g.) and α-naphthylisocyanate (2 c.c.) were heated together on steam bath and the light brown product which separated was extracted with petroleum ether (6 c.c.). Most of the derivative went in solution and after cooling the extract for several hours only a small quantity of the derivative^(XXII) separated (m.p. 95-97°C.). The dissolved urathane was recovered by distilling off petroleum ether, when a brown pasty substance was left.

Properties of the wetting agents prepared from cashew nut shell oil:

Qualitative stability tests:

Stability to alkali: The test was carried out as described

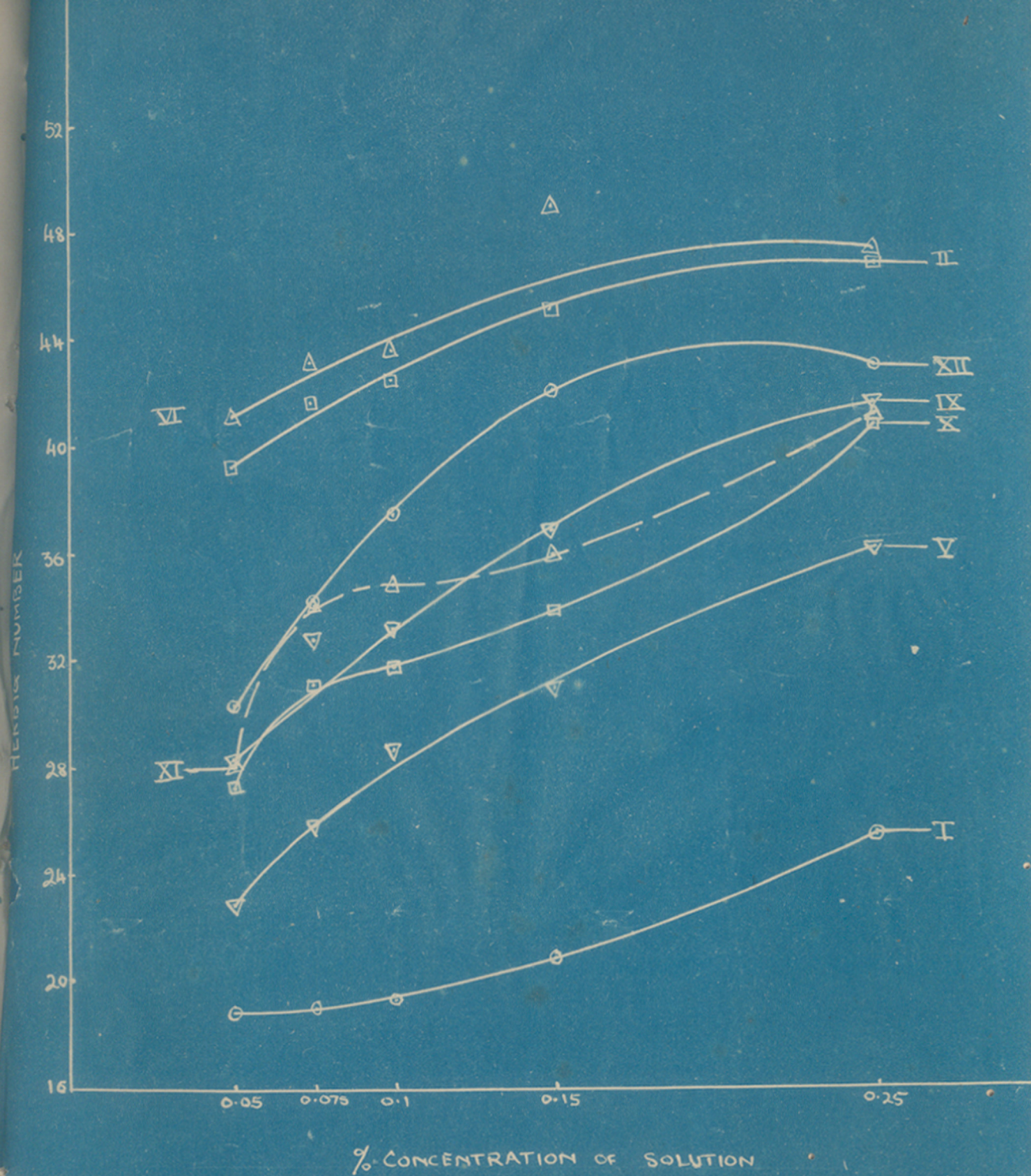


Fig. IX.

Wetting power of cashewnut shell oil derivatives

on page 83. All the compounds gave clear solutions in cold and on boiling.

Stability to mineral acids: The compounds were stable in cold and on boiling.

Stability to hard water: Compounds (XI) and (XII) gave slightly turbid solutions, but the other compounds were stable to hard water.

Determination of wetting power: The Herbig number was determined at 0.25, 0.15, 0.1, 0.075 and 0.05 % concentrations, and the sinking time (Draves test) at 0.1 and 0.05% concentrations. The results are tabulated in Table X and graphically represented in Fig. IX.

Table X

Compound	Herbig number					Sinking time in secs.	
	0.25%	0.15%	0.1%	0.075%	0.05%	0.1%	0.05%
I	25.5	20.8	19.2	18.9	18.7	Above 180	
II	47.0	45.2	42.5	41.7	39.3	128	Above 180
V	36.3	30.9	28.7	25.8	22.8	Above 180	
VI	47.5	49.1	43.6	43.2	41.2	80	125
IX	41.8	37.0	33.2	32.8	28.3	Above 180	
X	40.0	33.9	31.7	31.1	27.3	150	Above 180
XI	41.3	36.0	34.8	34.1	28.1	Above 180	
XII	43.1	42.1	37.5	34.2	30.3	Above 180	

o-Methyltetrahydroanacardol-disodium sulphonate (VI) had the highest wetting power judged by both the Herbig number and flotation methods, and tetrahydroanacardoldisodium sulphonate was next in order. In either of these the decrease in wetting power with dilution was gradual. The compounds arrange themselves as follows according to the decreasing Herbig number:

0.25%:- (VI), (II), (XII), (IX), (XI), (X), (V), (I).

0.15%:- (VI), (II), (XII), (IX), (XI), (X), (V), (I).

0.1:- (VI), (II), (XII), (XI), (IX), (X), (V), (I).

0.075:- (VI), (II), (XII), (XI), (IX), (X), (V), (I).

0.05:- (VI), (II), (XII), (IX), (XI), (X), (V), (I).

Except for (IX) and (XI), the other compounds do not change their order of efficiency as the concentration is changed.

In majority of cases the tetrahydroanacardol compounds are better than the anacardol analogues. Contrary to expectation the sulphates of the β -phenoxyethanols were not better than the corresponding disulphonates, although these were nearly equally efficient. *o*-Methylethers of anacardol and tetrahydroanacardol gave superior wetting agents than the parent phenoxy compounds. Compared with the carboxylamides the derivatives of cashew nut shell oil were poor wetting agents.

Calcium soap dispersion:

Titration method: To the sodium oleate solution (20 c.c.

of 2.3%) 1 solution of wetting agent (5 c.c.) was added, followed by calcium chloride solution (25 c.c. of 0.34%), filtered and washed as described in the previous pages (101-103). Net dispersion is recorded in Table XI.

Point light method: The solution of wetting agent (2 c.c. of 1%) and sodium oleate (10 c.c. of N/50) were mixed, followed by solutions of calcium chloride of varying strengths and the point light observed as usual (cf. page 106). The critical concentration of calcium chloride required is given in Table XI.

Table XI

<u>Compound</u>	<u>Net dispersion</u>	<u>Point light method</u> <u>% conc. of calcium chloride.</u> <u>solution</u>
I	15.2	0.303
II	7.3	0.302
V	12.0	0.169
VI	13.0	0.740
IX	4.9	0.17
X	11.9	0.584
XI	7.0	0.28
XII	8.6	0.438

Anacardoldisodium sulphonate (I) gave maximum dispersion and tetrahydroanacardol-o-methyletherdisodium sulphonate was next in order; but judged by the point light method the latter

was the best. The **compounds** may be arranged according to the following decreasing order of efficiency:

Titration method: (I), (VI), (V), (X), (XII), (II), (XI), (IX).

Point light method: (VI), (X), (XII), (I), (II), (XI), (IX), (V).

It will thus be seen that the results by the two methods could not be correlated. Except for anacardoldisodium sulphate (I), which was better than hydrogenated analogue(II), in all other cases the hydrogenated derivatives were more stable to hard water. No definite conclusion could be drawn about the comparative efficacy of sulphated and sulphonated derivatives. In general it was observed that cashew nut shell oil derivatives were superior calcium soap dispersing agents to carboxylamides.

Protective colloidal action:

Congo Rubine number: The determination was made as described in carboxylamides (page 108) The results are recorded in Table XII.

β -Tetrahydroanacardoxyethanoldisodium sulphate (XII) was best and the others range as follows: (VI), (V), (II), (XI), (X), (IX), (I).

Table XII/

Table XII

<u>Compound</u>	<u>Amount of wetting agent in mg.</u>
I	100
II	30
V	11.8
VI	10
IX	90
X	80
XI	55
XII	6

In all the cases the tetrahydroanacardol derivatives were better than the corresponding anacardol compound. In majority of cases the modification of the phenoxyhydroxyl by converting into o-methyl ether or by condensing with ethylene chlorhydrin gave better protective colloids.

Determination of antiseptic power:

The cloth method: The different wetting agents prepared were tested for antiseptic power by the "cloth method" described earlier (Gandhi and Venkataraman, loc. cit.). The finishing mixture was prepared in a test tube, fitted with a stirrer, to which a standard aqueous solution of the wetting agent (12.5 c.c.) to be tested was added, followed by wheat flour paste (12.5 c.c. of 5% paste). The mixture was raised to

65-70°C. with constant stirring by heating in a water bath, and a 2" square piece of bleached pugree cloth was inserted inside the paste and left in for 15 minutes. The piece was squeezed in a padding mangle, giving about 100% squeeze and air-dried in air. From each piece two pieces of one sq. inch were cut, treated with a drop of mildewed water at the centre and placed in a desiccator over mildewed water. The observations regarding the growth of mildew were made after 96 hours. The inhibition concentration was taken as the per cent concentration (on volume) of the antiseptic in the medium at which no stains or growth of organism was visible after 96 hours.

During the testing yellow, brown, olive-green and black stains appeared on the cloth treated with lower concentrations of the antiseptic, and as the concentration increased, the stains disappeared, until at the inhibition concentration they were absent. The maximum concentration of the standard wetting agent solution employed was 2%, due to insolubility of some of the wetting agents above 2% and less quantity of the compounds that could be spared for this test in the case of others. Hence inhibition concentrations below 1% could only ^{be} determined, and substances having lower antiseptic action being indicated only as inhibition concentration above 1%.

The results of these determinations are recorded in Table XIII.

Table XIII

<u>Compound</u>	<u>Inhibition concentration on cloth</u> (% on vol.)	
I	Above	1.0
II		0.2
V	Above	1.0
VI		0.3
IX	Above	1.0
X		0.6
XI	Above	1.0
XII		0.3
Product Y	Above	1.0
*Salicylanilide		0.01
*Zinc chloride		1.40
*Copper sulphate		0.2

(* J. Ind. Chem. Soc., Indl. Ed., 1942, 5, 8).

It was observed that the tetrahydroanacardol derivatives were not only better than anacardol compounds, but were better than zinc chloride, the commonly employed antiseptic in the textile industry. These were, however, less efficient than salicylanilide (Shirlan). Anacardol derivatives were

poor antiseptics. The modification of the phenoxy hydroxyl group in tetrahydroanacardol disodium sulphonate (II) made little change in antiseptic action, although the phenoxy compound (II) was better than (VI). Product Y also had poor antiseptic properties.

Summary

The present work represents further synthetical experiments in the programme of study of the relation between chemical constitution and properties, such as wetting, resistance to hard water and protective colloidal action of textile auxiliary agents carried out in this laboratory. The synthetic scheme has been based on the model of oleyl-N-methyltaurine (Product Y), which is one of the most widely used textile auxiliary agent. Thus, a series of wetting agents were prepared by condensing different fatty acids with arylamine sulphonic acids and their wetting and other properties examined to gauge their usefulness as textile auxiliary agents.

With a view to studying the influence of a C-alkoxy group in the benzene ring, p-anisidine and p-phenetidine sulphonic acids were condensed with lauric and oleic acids, and compared with the corresponding aniline sulphonic acid condensates.

In view of the outstanding properties of lauryl-p-toluidide-2-sodium sulphonate, a series of wetting agents were prepared by condensing p-toluidine-2-sulphonic acid with myristic, palmitic and stearic acids and mixed fatty acids from cocoanut, groundnut, cotton seed and mowhra oils. These products were, however, less efficient than the lauryl

derivatives. To study the influence of the relative positions of C-alkyl and amino groups in the benzene ring, acyl derivatives of ortho-toluidine-4-, and -5-sulphonic acid were prepared.

As C-alkylation gave generally superior agents, higher wetting alkylated carboxylamides were prepared by condensing m-4-xylidine-5- and -6-sulphonic acids and cumidine sulphonic acids with the fatty acids and the influence of introduction of increasing number of alkyl group in the aromatic ring observed.

In the different wetting agents prepared the influence of the relative positions of sulphonic and carboxylamide groups was studied. As cocconut oil fatty acids contain lauric acid as the main constituent, it was used in preparing acyl derivatives in addition to lauric and oleic acids. Although lauric acid derivatives were better wetting agents, the mixed fatty acid derivatives also had good all round properties and were considerably cheaper.

In addition to the standard procedure for the condensation of fatty acids chlorides and arylamine sulphonic acids in pyridine solution, it has been found feasible to effect the condensation in acetone, and in aqueous solution in the presence of alkalies like sodium carbonate and caustic soda. The general method followed was similar to B.P. 452,139, in

which the condensation of p-phenetidine-2-sulphonic acid and oleyl chloride in aqueous alkaline solution is described. A series of acid chlorides (e.g. lauryl, oleyl, myristyl, palmityl and stearyl chlorides and chlorides from mixed fatty acids of vegetable oils) were successfully condensed with arylamine sulphonic acids like anisidine, phenetidine-, and p-toluidine-, m-4-xylylidine- and cumidine-sulphonic acids, in aqueous alkaline solution.

Since a good wetting agent will act as a good detergent if it can reduce the interfacial tension, the measurement of this property is of great importance. The lowering of interfacial tension in terms of drop number with progressive increase in concentration of the solution of the wetting agent was studied in the case of three typical wetting agents, Igepon T, Nekal BX and sodium laurate. The effect of the rate of drops on the drop number was also observed.

The chief drawback of fatty acid soaps, as textile auxiliary agents, is their instability to hard water. The titration method for determining their calcium soap dispersing power was unsuitable as the soaps themselves combined with calcium chloride. Hence the soap and calcium chloride were mixed in equimolecular proportions, and the dispersed calcium soap determined, from the point of view of the relation between the length of the fatty acid chain and the dispersibility of the calcium soaps.

Sulphamic acid was used for sulphonating p-anisidine and p-phenetidine, when the sulphonic group was found to enter o- to the amino group.

To study the orientation of the sulphonic group in unsubstituted arylamines, aniline was sulphonated with sulphamic acid. The sulphonate acid obtained was characterised by preparing the p-toluenesulphonyl derivative and the p-chloraniline salt of the p-toluenesulphonyl derivative which were found to be identical with the corresponding derivatives from sulphanic acid. It was therefore concluded that in sulphonating with sulphamic acid the sulphonic group was directed to the p-position to the amino group and to the o- position if the p-position is already occupied.

Derivatives of cashew nut shell oil: Anacardic acid, the main constituent of cashew nut shell oil, has marked wetting and detergent properties. The Herbig number of a 0.5% solution of sodium anacardate was 62.2, which is of the same order as the figures for the commonly employed wetting agents. Hence the usefulness of cashew nut shell oil as a raw material to prepare wetting agents was studied.

The practical utilisation of sodium anacardate, in spite of its good wetting power, is limited on account of its sensitivity to hard water, due probably to the carboxyl group present. In the present work anacardol and tetrahydroanacardol were used as starting materials for synthetical experiments.

Anacardol and tetrahydroanacardol were solubilised by sulphonating with fuming sulphuric acid, when disulphonates were obtained. Similarly the disulphonates of o-methyl ethers of anacardol and tetrahydroanacardol were prepared. By condensing with ethylene chlorhydrin the phenoxyethyl alcohols from anacardol and tetrahydroanacardol were prepared and sulphonated with fuming sulphuric acid to give the disulphonates and with chlorosulphonic acid to give the phenoxyethyl sulphates. These compounds were evaluated for the wetting and other properties. To characterise the phenoxyethyl alcohols as distinct from the parent phenols, the 3:5-dinitrobenzoates, α -naphthylurathanes and p-toluenesulphonyl derivatives were prepared.

These newly synthesised compounds were found to be ~~be~~ poor wetting agents compared with the carboxylamides, although they are excellent calcium soap dispersing agents. The antiseptic properties of these products were also determined.

List of compounds

I	Lauryl- <u>p</u> -anisidide-3-sodium sulphonate
II	Oleyl- <u>p</u> -anisidide-3-sodium sulphonate
III	Lauryl- <u>p</u> -anisidide-2-sodium sulphonate
IV	Oleyl- <u>p</u> -anisidide-2-sodium sulphonate
V	Lauryl- <u>p</u> -phenetidide-3-sodium sulphonate
VI	Oleyl- <u>p</u> -phenetidide-3-sodium sulphonate
VII	Lauryl- <u>p</u> -phenetidide-2-sodium sulphonate
VIII	Oleyl- <u>p</u> -phenetidide-2-sodium sulphonate
*IX	Lauryl- <u>p</u> -toluidide-2-sodium sulphonate
X	Myristyl- <u>p</u> -toluidide-2-sodium sulphonate
XI	Palmityl- <u>p</u> -toluidide-2-sodium sulphonate
XII	Stearyl- <u>p</u> -toluidide-2-sodium sulphonate
*XIII	Oleyl- <u>p</u> -toluidide-2-sodium sulphonate
XIV	Condensation product of cocoanut oil fatty acids and <u>p</u> -toluidine-2-sulphonic acid.
XV	Condensation product of cotton seed oil fatty acids and <u>p</u> -toluidine-2-sulphonic acid.
XVI	Condensation product of groundnut oil fatty acids and <u>p</u> -toluidine-2-sulphonic acid.
XVII	Condensation product of mowhra oil fatty acids and <u>p</u> -toluidine-2-sulphonic acid.
XVIII	Lauryl- <u>p</u> -toluidide-4-sodium sulphonate
XIX	Oleyl- <u>o</u> -toluidide-4-sodium sulphonate

- XX Condensation product of cocoanut oil fatty acids
 and o-toluidine-4-sulphonic acid
- XXI Lauryl-o-toluidide-5-sodium sulphonate
- XXII Oleyl-o-toluidide-5-sodium sulphonate
- XXIII Condensation product of cocoanut oil fatty acids and
 o-toluidine-5-sulphonic acid.
- XXIV Lauryl-m-4-xylylidide-6-sodium sulphonate
- XXV Oleyl-m-4-xylylidide-6-sodium sulphonate
- XXVI Condensation product of cocoanut oil fatty acids and
 m-4-xylylidine-6-sulphonic acid
- XXVII Lauryl-m-4-xylylidide-5-sodium sulphonate
- XXVIII Oleyl-m-4-xylylidide-5-sodium sulphonate
- XXIX Condensation product of cocoanut oil fatty acids and
 m-4-xylylidine-5-sulphonic acid
- XXX Laurylcumidide-sodium sulphonate
- XXXI Oleylcumidide-sodium sulphonate
- *XXXII Laurylanilide-m-sodium sulphonate
- *XXXIII Oleylanilide-m-sodium sulphonate
- Product Y Igepon T

(* These compounds have already been previously prepared, Shirolkar and Venkataraman, J. Soc. Dyers Col., 1941, 57, 44. They are included here for comparison).

Derivatives of cashew nut shell oil

- I Anacardoldisodium sulphonate
- *II Tetrahydroanacardoldisodium sulphonate
- III Anacardol-o-methyl ether
- IV Tetrahydroanacardol-o-methyl ether
- V Anacardol-o-methyletherdisodium sulphenate
- VI Tetrahydroanacardol-o-methyletherdisodium sulphonate
- VII β -Anacardoxyethyl alcohol
- VIII β -Tetrahydroanacardoxyethyl alcohol
- IX sodium β -Anacardoxyethyl sulphate
- X sodium- β -~~T~~Tetrahydroanacardoxyethyl sulphate
- XI β -Anacardoxyethanoldisodium sulphonate
- XII β -Tetrahydroanacardoxyethanoldisodium sulphonate
- XIII β -Anacardoxyethyl-3:5-dinitrobenzoate
- XIV β -Anacardoxyethyl- α -naphthylurathane
- XV p-Toluenesulphonyl- β -anacardoxyethyl alcohol
- XVI β -Tetrahydroanacardoxyethyl-3:5-dinitrobenzoate
- XVII β -Tetrahydroanacardoxyethyl- α -naphthylurathane
- XVIII p-Toluenesulphonyl- β -tetrahydroanacardoxyethyl alcohol
- XIX Anacardoxy-3:5-dinitrobenzoate
- XX Tetrahydroanacardoxy-3:5-dinitrobenzoate

- XXI Anacardoxy- α -naphthylurathane
XXII Tetrahydroanacardoxy- α -naphthylurathane

{* This compound has been prepared previously
(Gandhi, Ph.D. Thesis, Univ. Bombay) and is included here
for comparison.

As required according to O. 215E, Handbook of the University of Bombay, I have mentioned the sources from which the information has been derived and reference to the literature of the subject, on which the present is based in the introductory part of the thesis. General guidance has been received from Dr. K. Venkataraman, D.Sc.(Manc.), F.I.C., A.M.I.Chem.E., Mody Professor of Chemical Technology, The University, Bombay. I take this opportunity of expressing my deep sense of gratitude to him for his inspiring guidance.

Candidate

B. D. Jilani

University
Teacher

K. Venkataraman

3rd June 1943