EUROPEAN QUALIFYING EXAMINATION 1997

PAPER A
CHEMISTRY

This paper comprises:

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INSTRUCTIONS TO CANDIDATES

You are to assume that you have received the annexed letter from your client including a descript an invention for which he wishes you to obtain a European patent together with references to the m pertinent prior art known to your client.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is to draft an independent claim (or claims) offering the applicant the broadest protection possible while at the same time having a good chance of succeeding before the EPO. In drafting your claim(s) you should bear in mind the need for inventive step over the prior art indicated, the requirements of the Convention, in particular as to the form of claims, and the recommendations made in the Guidelines for Examination in the EPO. Dependent claims should also be drafted so as to enable you to fall back upon them should the independent claim(s) fail and should be kept to a reasonable number.

You are also expected to draft an introduction, i.e. that part of the description which precedes the examples or the explanation of the drawings. The introduction should be sufficient to provide support for the independent claim(s), for example, by referring to selected portions of your claims. In particular, you should consider the advisability of mentioning advantages of the invention in the introduction.

You are expected to draft claims and an introduction for one European patent application only. This application should meet the requirements of the Convention as to unity. If you would in practise seek to protect further inventions by filing one or more separate applications, you should, in a note, clearly identify the subject-matter of the independent claim of such separate application(s). However, it is not necessary to draft the wording of the independent claim for the or each separate application.

In addition to your chosen solution, you may - but this is not mandatory - give, in a note, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such note should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who - after having filed such a request when enrolling for the examination - give their answer in a language other than German, English or French.

CLIENT'S LETTER

Dear Sir or Madam,

we are a small research institute looking on behalf of our clients for new solutions to their technical problems.

At present we are working on emulsifiers on behalf of a client, which emulsifiers should have the widest possible range of applications. These include applications in the cleansing agent industry, in the production of polymer fibres and yarns, in oil recovery and in the field of building materials and construction. Our client intends to have these emulsifiers manufactured by third companies. Therefore patent protection is so important to us to protect our interests. By the way, our client has given his consent to our filing a patent application in our name.

On the basis of the literature, sulphonated compounds seemed very promising since they are versatile and can be produced easily and at low cost. That is why we have chosen this field. We have found a number of products with properties which can easily be varied. By chance we have also discovered an interesting and simplified process for their manufacture.

So far we have not been able yet to sufficiently characterise our products. However, we think that the data enclosed will suffice to identify the products since simple, commercially available starting materials have been employed and well-known organic reactions utilised. Please file the application with the patent office before the end of this month.

We enclose the literature known to us (**Documents I** and **II**) which describe two important classes of widely known emulsifiers, i.e. nonionic and anionic. You may find this information useful.

Document I relates to nonionic emulsifiers.

As can be seen from **Document II**, it is known to sulphonate aromatic compounds using conc or fuming sulphuric acid. Due to the serious disadvantages these old processes entail, they are no interest to us or our clients and will probably soon have to be completely replaced. However, the products are widely used because of their advantageous emulsifying properties. We have found that almost all the disadvantages of the sulphonation process described in the **Document II** can be avoided by employing gaseous sulphur trioxide ($\mathbf{SO_3}$). We have also found by titration that sulphonation of a specific alkyl benzene always yields the same product regardless of whether the sulphonating agents known from **Document II** are used or $\mathbf{SO_3}$.

We have now found compounds which are very versatile because they combine the advantageous properties of both these known classes of emulsifiers.

The new emulsifiers are produced exclusively from para-alkyl phenols having the formula (p-$\mathbf{R\text{-}C_6H_4\text{-}OH}$), also known as 1-hydroxy-4-alkyl benzenes. A wide range of products can be manufactured from these **starting materials**, said products differing, according to the clients' requirements, in water-solubility, in compatibility with water hardness, in compatibility with basic and acidic media (pH) and in compatibility with salt water. To our knowledge, these starting materials have not yet been used in this field. We have limited our research to these compounds because they cover completely the required broad range of properties and we do not know if benzenes substituted in the 1,2- or 1,3-positions can be satisfactorily employed in the same way. As a precaution, any compounds not falling under the formula cited above should therefore be disregarded.

The para-alkyl phenols can be employed individually or in the form of mixtures of such compounds having different alkyl groups. They are commercially available. The alkyl groups **R** of our starting materials have 6 to 24 carbon atoms. Outside this range the desired well-balanced properties cannot be achieved since the hydrophobic portion of the compound is either too small or too large. Linear alkyl groups having 8 to 16 carbon atoms have proved to be especially advantageous. The best results as regards the properties important for emulsifiers are achieved with products made from commercially available technical mixtures of homologous alkyl phenols, the average number of carbon atoms in the alkyl groups being 10 to 14.

These compounds undergo two different and independent reactions, i.e. with alk (oxyalkylation) on the one hand and with SO_3 (sulphonation) on the other. Oxyalkylation (oft alkoxylation) can be carried out before or after sulphonation. The aim of the reactions is to y compounds having one anionic group. This can be verified by means of titration of the product obtained.

Purely for reasons of simplicity, (i) the starting compound, i.e. the alkyl phenol, and (ii) the product of its reaction with alkylene oxide or sulphur trioxide obtained in the first of the two reactions mentioned, will hereinafter be called "substituted benzene".

The **oxyalkylation** will be described first. In the course of this reaction the substituted benzene is reacted with an alkylene oxide having the simplified overall formula $\mathbf{R^1O}$ wherein $\mathbf{R^1 = -CH_2\text{-}CHR^2\text{-}}$ and $\mathbf{R^2 = -H, -CH_3}$ and $\mathbf{-C_2H_5}$, i.e. ethylene oxide, propylene oxide and butylene oxide or a mixture of those alkylene oxides, at a temperature of 100 to 150°C, the molar ratio of oxide to substituted benzene being 2 to 10. For safety reasons we have always employed pressures of from 0.4 to 0.6 MPa in our test apparatus (alkylene oxides are extremely toxic). In the course of the reaction, the alkylene oxide molecules are added to the terminal hydroxy groups, i.e. to the phenol group itself or to the glycol ether (or oxyalkylate) groups already added thereto. This reaction and its products are well known as such to the expert, see **Document I**. Ethylene oxide is the alkylene oxide most widely used and produces oligo- and polyoxyethylate groups (often called polyethoxy or polyoxyethylene) which render the product hydrophilic or even water-soluble. Probably owing to their additional alkyl groups, propylene oxide and butylene oxide render the products more hydrophobic. Products exactly having the degrees of hydrophilic or hydrophobic properties as desired can therefore be made by copolymerising or block copolymerising ethylene oxide with other alkylene oxides.

Sulphonation can be carried out before or after the oxyalkylation described above. Sulphonation of organic compounds is generally known to the expert, see **Document II**. For this reason only a few decisive features will be discussed here. As mentioned above, we have found that the reaction with gaseous sulphur trioxide is more advantageous than that with concentrated or fuming sulphuric acid (oleum). Compared with these other sulphonating agents, sulphonation with $\mathbf{SO_3}$ has the great advantage

that no waste sulphuric acid is produced. As a result, high-grade steel can be used as reacto
and the reaction rate is much faster. Nor does any waste acid, for example, have to be disposed

Owing to the high reaction rate and strong heat generation, however, intensive mixing and effective cooling is necessary. To avoid overheating, sulphur trioxide is exclusively used in a form diluted with a carrier gas, e.g. air or nitrogen, to a concentration of 4 to 8% by volume. Such a mixture is produced, for example, by the known combustion of sulphur and subsequent contact process. The reaction can be carried out continuously or discontinuously. Suitable reactors are known, e.g. bubble-cap columns and annulus reactors. We are, however, not interested in questions of engineering and process technology, such as the form of the reactor and the type of mixing, and these questions are of no importance for our invention. What is essential, however, is that the reaction conditions found by us and stated in this letter are strictly adhered to.

SO_3 is added in such a way that an excess of 3 to 10 mol% is employed in the reaction, based on the equimolar amount theoretically necessary to add one molecule of **SO_3** to each benzene ring. Titration of the products has confirmed that the reaction always yields compounds having one acid group per molecule.

The reaction temperature should under no circumstances exceed 135°C because otherwise too many impurities are formed which are difficult to remove. Temperatures up to 80°C have proved to be advantageous, because the heat of reaction can then be controlled particularly well. This is apparent, for example, from the greater purity of the product - most easily apparent from its lesser discolouration. This is also an important advantage of our process as compared with the use of concentrated or even fuming sulphuric acid which always yields highly discoloured products. When alkyl phenols are sulphonated, a minimum temperature of 60°C proved to be efficient.

The other embodiment of the process is even more advantageous as far as temperature control is concerned. When oxyalkylated alkyl phenols are sulphonated, temperatures of 30 to 50°C are sufficient to ensure a satisfactory reaction rate. Especially in this second embodiment, temperatures should not exceed 80°C since otherwise the yield decreases. This embodiment of the process is therefore especially advantageous because emulsifiers can thus be manufactured with practically no disco[illegible] process in which the reaction is easier to control.

The reaction time for the sulphonation depends partly on the reactor geometry and partly on other parameters, and can extend from a few minutes to several hours. A process engineer can easily optimise this.

Directly after sulphonation, the sulphonated reaction product is neutralised because we have observed that some compounds do not remain stable for long in acidic media, especially at higher temperatures. At all events, decomposition must be avoided. For neutralisation, the product is preferably mixed with a solvent. Suitable solvents are, for example, xylene, kerosene and diesel fuel. The well mixed solution is neutralised by slow addition of a basic compound. Oxides, hydroxides and bicarbonates of alkali metals can be employed. Sodium and potassium oxides are especially worth mentioning, and even more preferred are their respective hydroxides, because they are easy to obtain and to handle. The hydroxides can be added as 30 to 60% by weight solutions. The course of the neutralisation can be easily monitored by measuring the pH. The salts formed are products of a strong acid and a strong base and therefore are neutral. Thus, a pH of about 7 indicates the end of the reaction. During neutralisation the temperature is usually held at 20 to 135°C; higher temperatures can lead to more discolouration. In addition, temperatures above the boiling point of water, i.e. above 90 to 100°C, are advantageous because the azeotropic mixture of water and xylene can then be distilled off when xylene is used as the solvent. This makes the subsequent drying stage at temperatures of 120 to 160°C, which would otherwise be necessary, no longer necessary. For this reason, xylene is preferred as the solvent.

Depending on the requirements of the various fields of application, emulsifiers having finely determined properties and advantageously combining the properties of anionic and nonionic emulsifiers can be prepared by selecting the starting materials and the reaction steps mentioned above. The usual cloud points of nonionic emulsifiers can thereby be "shifted" outside the temperatures of application so that they no longer appear to exist. This is especially true for mixtures of homologous compounds in which the chain lengths of the alkyl group (see above) and of the oxyalkyl group (as described below) can diverge to a certain extent from a mean value. These emulsifiers are also less sensitive to the of electrolytes.

It is possible to produce either completely water-soluble or completely oil-soluble emulsifiers or those with a solubility lying somewhere inbetween. When these compounds are used as solubilisers, clear solutions can be obtained even when the substances to be dissolved are generally insoluble in the solvent. Oil-in-water and water-in-oil emulsions can be formed when these compounds are used as emulsifiers. The compounds can also serve as lubricants in the polymer fibre and yarn industry and can easily be washed out after application.

It should also be pointed out that products first sulphonated then oxyalkylated are considerably more stable in acid media than those sulphonated after oxyalkylation. The compounds produced according to the second embodiment of the process appear to decompose much more easily than those according to the first embodiment under acidic conditions and/or at high temperatures, e.g. above 120°C. This could also cause the above-mentioned decrease in yield at high temperatures.

As can be seen from the above description of the process, the emulsifiers according to our invention show in part pronounced temperature stability. Lack of stability manifests itself usually by the fact that the prepared emulsions break, the solutions become cloudy and/or components of those solutions or emulsions are even precipitated when the temperature is raised or the pH is decreased. If the starting materials and the molecular weight, determined by cryoscopy, are known, the degree of oxyalkylation (the number of oxyalkylate units in the oligoether chain) can be calculated. This ranges from **n** = 1 to 10, mostly from **n** = 1 to 4. Homologous mixtures with an average value of **n** ranging from 2 to 4 are preferred.

In the attached examples, the properties of some of the compounds are indicated, because the principal properties can thus be best demonstrated. As has already been mentioned, mixtures of homologous compounds are preferred for use in practice, i.e. mixtures of compounds made from the same starting materials, the chain lengths of **R** and the degree of oxyalkylation **n** varying around an average value.

The emulsifiers can be successfully employed in widely different fields of application. Th tertiary oil recovery, the building industry (particularly concrete construction), emulsion polyme and the polymer fibre and yarn industry. As has already been mentioned above, a certain spectrum product properties can be achieved, ranging from oil-soluble to water-soluble. Depending on the field of application, thermal properties and stability against acids should also be considered. This applies in particular to emulsifiers used at a low pH value (e.g. < 6.5) and at temperatures above 120°C.

In enhanced oil production (secondary and tertiary oil recovery), water or an aqueous salt solution (brine) is usually injected into the rock formations containing oil to displace the oil. This process is known to the expert. The previous methods of oil recovery, the type of rock, its temperature, its depth and other factors known to the expert have then to be taken into account. Often, the rock formations containing oil have temperatures near or above 125°C, saltwater is used, and/or the rock formations concerned contain salt.

According to our invention it is possible to add emulsifiers to the aqueous medium in such processes in amounts of usually up to 10% by weight. In most cases, 1 to 6% will suffice. The water or brine is mixed thoroughly with the emulsifier or mixture of emulsifiers and then injected into the rock formation through one or more bore holes.

In addition, conventional textile lubricants, e.g. for the manufacture of polymer fibres and threads can be improved using our emulsifiers. The emulsifiers are added to the usual lubricants in amounts of 1 to 10 (normally 2 to 5)% by weight. The emulsifiers give the products excellent lubricious and antistatic properties, good winding properties even at high thread velocities and abrasion resistance on metal parts. The other ingredients of these lubricants are usually purified mineral oils, synthetic fatty acid esters or polyoxyalkylene glycols. This list is not exhaustive. These and other lubricants are known to the expert.

Another interesting application is the addition of our emulsifiers to concrete. The workability of the concrete is thus improved. The water-cement ratio can thus be diminished, the amount of fine additives (aggregate) reduced and the pumpability of the concrete increased. Moreover, the emulsifier acts as an air-entraining agent which is known to enhance strongly the resistance of the hardened conc

to frost and water. For this application, the emulsifier is added in amounts of 1 to 10, preferably 2 to

by weight of the concrete.

The emulsifiers are also highly suitable for emulsion polymerisation or microsuspension polymerisation of ethylenically unsaturated monomers, e.g. vinyl halides, styrenes or vinyl esters. The particle sizes of the polymers can, as usual, be adjusted by means of the amount of emulsifier added. The amounts usually employed are 0.1 to 5% by weight of the aqueous phase.

<u>Example 1</u> Oxyethylation and subsequent sulphonation

Ten moles (2204 g) of para-nonyl phenol were dissolved in 10 l of xylene and changed to a stirred autoclave under nitrogen as protective gas. After heating to 120°C, 40 moles (1600 g) of ethylene oxide were added at a pressure of 0.5 MPa. The temperature was kept in the range of 120 to 130°C until the pressure had dropped to 0.11 MPa. The product was flushed with nitrogen and then reacted with sulphur trioxide (4% by vol. of $\mathbf{SO_3}$ and 96% by vol. of nitrogen) at a temperature of 35°C in a glass reactor with intensive stirring until an amount of 840 g (10.5 moles) of sulphur trioxide had been absorbed. Subsequently the mixture was neutralised slowly (so that the temperature did not exceed 110°C) by addition of aqueous sodium hydroxide, the water being largely removed by distilling off the azeotrope xylene/water. The product had an acid number of 117.6. This corresponds to one acid group per molecule.

<u>Example 2</u> Sulphonation and subsequent oxyethylation

In this example, the same amounts of the same compounds as in Example 1 were employed. However, in this example the sulphonation as a first step took place at 70°C under otherwise identical conditions. The subsequent reaction steps - neutralisation and oxyethylation - were carried out as in Example 1. The product had an acid number of 117.5, i.e. in this case also one acid group was present per molecule.

Example 3

In this example, the properties of the emulsifiers produced according to the preceding examples described (see Table 1). Each of the compounds contained one acid group neutralised using aqueous sodium hydroxide. In the case of EO/PO-emulsifiers, propylene oxide was added after the addition of ethylene oxide. Stable emulsions were formed from 100 ml of distilled water, 10 ml of paraffin oil and 0.1 ml of emulsifier. To these emulsions, 10 ml of an aqueous 2% by weight calcium chloride solution were added dropwise with slow stirring. In the table, "+" indicates that the emulsion remained stable and "-" that it separated into an aqueous phase and an oil phase.

The stability of the emulsifiers in an acidic aqueous phase was also determined. For this purpose, solutions containing 0.1% by weight of emulsifier were prepared, their pH-values were adjusted to 3, and 10 ml of a 2% by weight barium chloride solution was added. The samples were then heated for 2 hours to 120°C in closed vessels to determine whether barium sulphate was precipitated. Apart from Sample **g** which turned slightly cloudy, the emulsifiers made according to Example 2 remained unchanged, whereas the ones made according to Example 1 showed significant to strong turbidity caused by barium sulphate.

Example 4

A technical homologous mixture called "para-dodecyl phenol" having an average number of C-atoms of 12 in the alkyl group **R** was sulphonated in a first step under the same conditions as in Example 2. After neutralisation (with aqueous sodium hydroxide) the product was reacted with ethylene oxide so that an average degree of oxyethylation **n** of 4 was achieved. The lubricity of the emulsifier was measured using a Baroid Lubricity Tester, the angular momentum of a 2.5% by weight aqueous solution of emulsifier being compared with that of water. The emulsifier caused a decrease of 58%.

Table 1

Sample	No. of C atoms in the alkyl group of the phenol	Process according to Example No.	Alkylene oxide		CaCl$_2$ solution
			Type	No. of units	
a	8	1	**EO**	4	+
b	12	1	**EO**	4	+
c	8	1	**EO/PO**	4/2	+
d	12	1	**EO/PO**	4/2	+
e	8	2	**EO**	4	+
f	12	2	**EO**	4	+
g	18	2	**EO**	4	+
h	18	1	**EO**	4	+
i*	12	-	-	0	-

EO = ethylene oxide **PO** = propylene oxide * Comparative test (without oxyalkylation)

We would ask you to file a patent application without delay, and in any event before the end of this month.

Yours faithfully,

The Inventors Ltd.

DOCUMENT I (State of the Art)

Nonionic tensides

The technically most important nonionic tensides are condensation products of hydrophobic alcohols, phenols, amines, carboxylic acids, carbonamides etc. with hydrophilic poly- or oligoglycol ethers. The polarity of the oxygen atoms bonded in the hydrophilic ether groups imparts water-solubility and surface active properties to the hydrophobic parent structure.

The poly- or oligoglycol ether groups can be produced by adding cyclic ethers, in particular, ethylene oxide (oxirane, 1,2-epoxy ethane, epoxide = cyclic ether of ethylene), propylene oxide (2-methyl oxirane, 1,2-epoxy propane) or butylene oxide (2-ethyl oxirane, 1,2-epoxy butane), to a free hydroxy group. The reaction is usually called oxyalkylation or alkoxylation.

Nonionic tensides are colourless substances with liquid consistency, but with increasing molecular weight they have a pasty to waxy consistency. They are much less sensitive to water hardness and other electrolytes than anionic tensides. The possible applications of nonionic tensides are universal, given the wide variability of their structure and thus of their properties. The solubility of nonionic tensides in water results from hydration of the oxygen groups by hydrogen bonding. The degree of hydration decreases with increasing temperature, and the water solubility of nonionic tensides therefore decreases with increasing temperature. In the case of tensides that dissolve in water to give a clear solution - e.g. oxyethylates with a fairly high degree of oxyethylation - turbidity and separation of a tenside phase immiscible with water occur at a specific temperature characteristic to each tenside. The temperature at which the turbidity occurs is the "cloud point" of the tenside at a specific concentration. On the other hand, since the solubility of tensides in water decreases on cooling, as is generally the case with solutions, a cloud point is also reached when the temperature is reduced.

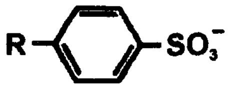
The solubility of nonionic tensides in water can be influenced not only by the degree of oxyethylation but also by incorporating higher alkylene oxides than ethylene oxide. The oxypropyl group obtained from propylene oxide is already hydrophobic. This property can be used to enlarge a hydrophobic structure prior to oxyethylation by adding propylene oxide. Furthermore, oxyalkylation can be perform with mixtures of ethylene oxide and propylene oxide to obtain - through the selection of the ratio of the amounts of the two epoxides and the alternating order in which these compounds are added etc. - various effects which will be merely referred to here in passing.

Oxyalkylation can be catalysed by means of acids (generally Lewis acids such as boron trifluoride, tin tetrachloride or antimony pentachloride) or bases (such as alkali metal, alkali metal oxide, alkali metal hydroxide or alkali metal alcoholate). The choice depends in particular on the acidity of the hydroxy compound used as the hydrophobic group and its reactivity and the intended length of the oxyalkylate chain. The process can also be started up with an acidic catalyst to cause as a first step the quantitative reaction of a hydroxy compound, which is less reactive than an oxyalkylate chain already formed, and then extend the chain length using a basic catalyst. The aim of any oxyalkylation is to produce a homologous mixture, since it has been shown that such mixtures have application properties superior to those of molecularly uniform substances.

A brief reference will be made here to the need to take appropriate safety precautions when handling epoxides which are known to be highly reactive, partly because of their high toxicity and the fire risk they represent.

Known examples of such nonionic tensides are para-octyl-, para-nonyl- and para-dodecylphenyl polyoxyethylates having 1 to 100 oxyethylate (ethoxylate) units per molecule, depending on the hydrophilic properties desired. Usually 4 to 25 units are sufficient to obtain a satisfactory emulsifying effect.

DOCUMENT II (State of the Art)



6.2 Sulphonates

Sulphonates are salts of sulphonic acids, in which a hydroxysulphonyl group **(-SO_3H)** is bonded via the sulphur atom directly to a carbon atom of the hydrophobic parent structure. This bond is thermally and chemically very stable. The strong affinity of the sulphonate group for water results in the sulphonates having good water solubility, which decreases with increasing equivalent weight, that is to say as the proportion of the hydrophobic part increases in relation to the hydrophilic sulphonate group. The alkaline-earth salts of sulphonic acids are less soluble in water than the alkali metal salts. The sensitivity of sulphonates to water hardness therefore increases with increasing equivalent weight. Being salts of strong acids and strong bases, the alkali and alkaline-earth sulphonates are neutral in aqueous solution.

Sulphonates are nowadays the most important group among the synthetic tensides. They are therefore used not only in detergents but also as outstanding solubilisers and dispersants. Solubilisers make virtually insoluble substances soluble or emulsifiable in a solvent, i.e they solubilise. This effect is known as hydrotropy when water is employed as the solvent. Some of these classes of compounds are suitable for improving the viscosity of concrete mixtures and drilling muds or improving the displacement of oil by pumping water into rock formations containing oil in tertiary oil recovery.

6.2.1 Alkylbenzene sulphonates

p-Alkylbenzene sulphonates having (on average) 8-20 carbon atoms in the alkyl group have a wide range of uses. p-Alkylbenzene sulphonates with less than 6 carbon atoms in the alkyl group are no longer surface-active. The compounds correspond to the formula $p\text{-}\mathbf{R\text{-}C_6H_4\text{-}SO_3}^{-}$ having the structure
The alkylbenzene sulphonates (=alkylphenyl sulphonates) are mainly used in the form of sodium salts, and occasionally also as potassium and ammonium salts. The octyl- to decylbenzene sulphonates have a good wetting ability, but are unsuitable as emulsifiers and cleansing agents due to the shortness of the hydrophobic group. The most universally usable alkylbenzene sulphonates are those with an average of about 12 carbon atoms in the alkyl chain, consisting of homologues with 10-14 carbon atoms

("dodecylbenzene sulphonate"). Because of their outstanding suitability as tensides in dete cleansing agents, dodecylbenzene sulphonates are nowadays the most important group of sy tensides in terms of quantity.

Alkylbenzene sulphonates with 15 or more carbon atoms in the alkyl group are sparingly soluble in water, but are readily soluble in organic media, e.g. mineral oil. Solutions in mineral oils play a particular role as drilling and cutting oils in the metal-processing industry, and e.g. as spinning oils in the textile, polymer fibre and yarn industries. In recent times, oil-soluble alkylbenzene sulphonates have come to the fore as tensides for tertiary oil recovery, although the concentration of salt or other electrolytes should be low since otherwise the emulsifying effect is often insufficient.

Alkylbenzene sulphonates are produced commercially by alkylation of benzene (Friedel-Crafts reaction) or by catalytic addition of olefins to benzene, followed by sulphonation of the alkyl benzene obtained and neutralisation. Sulphonation occurs at low temperatures (e.g. about 30°C) mostly in the para position and is carried out using concentrated sulphuric acid or oleum in acid-proof, usually leaded, mixing vessels, since the reaction mixture is highly corrosive. The reaction is described below using dodecylbenzene as an example:

$$C_{12}H_{25}\text{-}C_6H_5 + H_2SO_4 \rightarrow C_{12}H_{25}\text{-}C_6H_4\text{-}SO_3H + H_2O$$

Since sulphuric acid containing more than 10% water no longer reacts with alkyl benzene, care must be taken to ensure that the water concentration of the acid does never exceed that limit.

The alkyl benzene is initially charged and the acid is metered in. Stirring is terminated after 1 to 2 hours and the brown-coloured "waste acid" deposited is removed. The sulphonic acid is purified further by washing with 5 to 10% by weight of water at 80°C and removal of the resulting 70 to 75% sulphuric acid.

In carrying out neutralisation, usually only enough water is added to produce a flowable paste. The paste and the aqueous (sodium) hydroxide are then in the preferred procedure simultaneously and in a controlled manner metered in, and the reaction is followed by measuring the pH of the product and the temperature. A particularly advantageous method is to keep much of the neutralised product in a loop and add the sulphonic acid and aqueous (sodium) hydroxide before the mixture in the loop enters the mixing pump.