

EUROPEAN QUALIFYING EXAMINATION 1997

PAPER B CHEMISTRY

This paper comprises:

* Instructions to Candidates	97/B(C)/e/1
* Description of the Application	97/B(C)/e/2-11
* Claims	97/B(C)/e/12
* Communication	97/B(C)/e/13-14
* Document I (State of the Art)	97/B(C)/e/15-16
* Document II (State of the Art)	97/B(C)/e/17-18
* Document III (State of the Art)	97/B(C)/e/19-22
* Document IV (State of the Art)	97/B(C)/e/23
* Document V (State of the Art)	97/B(C)/e/24-25

INSTRUCTIONS TO CANDIDATES

In this paper, you should assume that a European patent application for all the Contracting States comprising the appended documents(*) has been filed and that the European Patent Office has issued the annexed official communication. The paper may include a client's letter containing instructions about the way your client wishes to prosecute the European patent application.

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 now to draft a full response to the official communication. The response should be a letter to the EPO, accompanied, if appropriate, by an amended set of claims. No amendments to the description should, however, be made.

The claims should afford the broadest protection possible while meeting the requirements of the Convention. In your letter of response you should set out your arguments in support of the patentability of the independent claim(s).

If you consider that any part of the application ought to be made the subject of one or more divisional applications, you should in a note, clearly identify the subject-matter of the independent claim of such divisional application(s), for example, by referring to selected portions of your claims. However, it is not necessary to draft the wording of the independent claim for the or each divisional 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.

(*) These documents do not necessarily constitute the only or best solution to the task set in Paper A.

DESCRIPTION OF THE APPLICATION

The present invention relates to emulsifiers with the widest possible range of applications. Reference is only made to the cleansing agent industry, to the production of polymer fibres and yarns, to oil recovery and to the field of building materials and construction.

- 5 More specifically, the invention relates to sulphonated products (hereinafter referred to as emulsifiers) which are very versatile as a result of their wide-ranging and easily varied properties. They can also be produced easily and at low cost. Moreover, a simplified process for their manufacture has been found.
- 10 The emulsifiers are based on simple, commercially available starting materials modified by means of conventional organic reactions. **Documents I and II** describe two important classes of widely known emulsifier, i.e. nonionic and anionic.

Document I relates to nonionic emulsifiers, the emulsifying capacity of which is markedly
15 temperature dependent, an increase in temperature usually causing a reduction in emulsifying capacity.

The class of anionic emulsifiers described in **Document II** does not have this temperature sensitivity, but they are quite sensitive to salts and other electrolytes. Nevertheless these sulphonated aromatic
20 compounds are widely used because of their advantageous emulsifying properties. As can be seen from the document, aromatic starting compounds have hitherto been sulphonated using concentrated or fuming sulphuric acid. Due to the serious disadvantages these old processes entail, they will probably soon have to be completely replaced. It has now been found that this reaction can be carried out better using gaseous sulphur trioxide (SO_3), thereby avoiding almost all the problems of
25 the sulphonation process described in the **Document II**. It has also been found by titration that using a specific alkyl benzene always yields the same product regardless of whether the sulphonating agents known from the **Document II** are used or SO_3 .

The disadvantages of the known emulsifiers can be avoided by using new compounds having a broad
30 field of application since they combine the advantageous properties of both the known classes of emulsifiers.

The subject-matter of the invention is new emulsifiers which can be produced by reacting a para-alkyl phenol having the formula $p\text{-R-C}_6\text{H}_4\text{-OH}$, wherein R is a $\text{C}_6\text{-}$ to $\text{C}_{24}\text{-}$ alkyl group, in two consecutive and separate reaction steps, one being the reaction with an alkylene oxide and the other the reaction with sulphur trioxide.

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The process for the production of these emulsifiers therefore consists of two reaction steps (a) and (b), which can take place in either order.

In reaction step (a) at least one alkylene oxide having the formula R^1O where $\text{R}^1 = \text{-CH}_2\text{-CHR}^2\text{-}$ and $\text{R}^2 = \text{-H, -CH}_3 \text{ and -C}_2\text{H}_5$, is reacted with the p-alkyl phenol or the product of reaction step (b) in a molar ratio of 2 to 10 at a temperature of 100 to 150°C.

In reaction step (b) sulphur trioxide SO_3 is added to the p-alkyl phenol or the product of reaction step (a) in a form diluted with a carrier gas at a temperature of up to 135° C in such a way that an excess of 3 to 5 mol% is used in the reaction, based on the equimolar amount theoretically necessary to add one molecule of SO_3 to each benzene ring.

The new emulsifiers are produced exclusively from para-alkyl phenols having the formula $(p\text{-R-C}_6\text{H}_4\text{-OH})$, 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 requirements - in water-solubility and in compatibility with water hardness, in compatibility with basic and acidic media (pH) and in compatibility with salt water. These starting materials have not yet been used in this field.

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 the 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 alkylene oxides (oxyalkylation) on the one hand and SO_3 (sulphonation) on the other. Oxyalkylation (often called alkoxylation) can be carried out before or after sulphonation. The aim of the reactions is to yield compounds having one anionic group. This can easily be verified by means of titration of the product
5 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".

10 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 R^1O , wherein $\text{R}^1 =$ $-\text{CH}_2-\text{CHR}^2-$ and $\text{R}^2 = -\text{H}$, $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$, 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
15 substituted benzene being 2 to 10. Since alkylene oxides are very toxic, certain safety precautions should be taken, the appropriate pressure to be employed having been found to be from 0.4 to 0.6 MPa in suitably configured apparatus. 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
20 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
25 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, the reaction is carried out with gaseous
30 sulphur trioxide instead of with concentrated or fuming sulphuric acid (oleum). Compared with these other sulphonating agents, sulphonation with SO_3 has the great advantage that no waste sulphuric

acid is produced. As a result, high-grade steel can be used as reactor material and the reaction rate is much faster. Nor does any waste acid, for example, have to be disposed of.

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. Questions of engineering and process technology, such as the form of the reactor and the type of mixing are not the subject-matter of the present invention. What is essential, however, is that the reaction conditions stated here 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 the present 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 has 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 discolouration in a process in which the reaction is easier to control.

- 5 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 it has been
10 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
15 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
20 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.

25

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 range of
30 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 presence of electrolytes.

- 5 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
10 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
15 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 this invention show in part pronounced temperature stability. Lack of stability manifests itself usually by the fact
20 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
25 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.

- 5 The emulsifiers can be successfully employed in widely different fields of application. These include tertiary oil recovery, the building industry (particularly concrete construction), emulsion polymerisation and the polymer fibre and yarn industry. As has already been mentioned above, a certain spectrum of 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
10 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
15 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.

- 20 According to the present 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.

- 25 In addition, conventional textile lubricants, e.g. for the manufacture of polymer fibres and threads can be improved using these 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
30 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 concrete parts to frost and water. For this application, the emulsifier is added in amounts of 1 to 10, preferably 2 to 5% 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.

Example 1 Oxyethylation and subsequent sulphonation

Ten moles (2204 g) of para-nonyl phenol were dissolved in 10 l of xylene and charged 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 SO₃ 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.

Example 2 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 are 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 the 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 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	
5	a	8	1	EO	4	+
	b	12	1	EO	4	+
	c	8	1	EO/PO	4/2	+
	d	12	1	EO/PO	4/2	+
10	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)

1. Process for producing emulsifiers by reacting para-alkyl phenol having the formula $p\text{-R-C}_6\text{H}_4\text{-OH}$, wherein **R** is a $\text{C}_6\text{-}$ to $\text{C}_{24}\text{-}$ alkyl group, in two separate reaction steps, in any order, **(a)** with alkylene oxide R^1O , where in $\text{R}^1 = \text{-CH}_2\text{-CHR}^2\text{-}$ and $\text{R}^2 = \text{-H, -CH}_3 \text{ or -C}_2\text{H}_5\text{,}$ and **(b)** with sulphur trioxide SO_3 , wherein
 - (a)** at least one alkylene oxide having the above formula is reacted with the para-alkyl phenol or the product of reaction step **(b)** in a molar ratio of 2 to 10 at a temperature from 100 to 150°C;
 - (b)** SO_3 is added to the alkyl phenol or the product of reaction step **(a)** in a form diluted with a carrier gas at temperatures up to 135°C in an excess of 3 to 10 mol% in relation to the equimolar amount theoretically necessary to add one SO_3 molecule to each benzene ring.
2. Emulsifier obtainable by reacting p-alkyl phenol according to the formula in Claim 1 in two consecutive, separate reaction steps with alkylene oxide and sulphur trioxide according to the process of Claim 1.
3. Use of the emulsifier according to Claim 2 in enhanced mineral oil recovery.
4. Use of the emulsifier according to Claim 2 in lubricants for the production of polymer fibres and yarn.
5. Use of the emulsifier according to Claim 2 as a concrete additive.
6. Use of the emulsifier according to Claim 2 in the emulsion or microsuspension polymerisation of ethylenically unsaturated monomers.
7. Process for sulphonating para-alkyl phenol having the formula stated in Claim 1 with sulphur trioxide according to reaction step **(b)** of Claim 1.

COMMUNICATION

1. **Document III (DIII)** clearly anticipates all the subject-matter of Claims 1 to 6 in its entirety. The claims do not therefore meet the requirements of Articles 52(1) and 54(1) and (2) EPC.
2. **DIII** describes emulsifiers which are derived from an alkyl phenol which is oxyalkylated and sulphonated in two consecutive reaction steps. The reaction conditions appear to correspond to those stated in the present application. Reference is made, for example, to the reaction temperatures. Where identical starting compounds are reacted under identical reaction conditions in the same way, it must be assumed that the reaction products are identical, as well.
3. The stated uses also appear to correspond precisely to those claimed in the present set of claims. This applies equally to the amounts of emulsifier suggested in the description.
4. Claim 7 is clearly anticipated by **Document IV (DIV)**. Reference need only be made in this connection to the description in that document of the sulphonation of para-dodecylphenol to the corresponding 2-hydroxy-5-dodecyl benzene sulphonic acid. The reaction conditions match the sulphonation conditions stated in the application.
5. **Document V (DV)** also describes compounds which fall within the wording of Claim 2. The present Claim 2 does not state the structure of the claimed compounds but instead defines the products by way of the process carried out. However, the fact that they are identical with the products of **DV** is clear for the skilled person. To support this argument, reference need only be made to the paragraph directly following the formula in **DV**.
6. In these circumstances, it would not seem possible in this communication to address any questions other than that of novelty (see also Guidelines C-IV, 9.1).
7. In addition, **DIV** shows that the sulphonation of aromatic compounds by sulphur trioxide has long been part of general technical knowledge.

8. According to the description, the neutralisation of the sulphonated product immediately after reaction step (b) appears to be an essential feature. This should be borne in mind if the claims are reformulated. The degree of oxyalkylation also appears to be an essential feature of the claimed compounds.
9. If you wish to continue with the application, you are invited to submit claims which take the aforementioned objections into account and comply with the requirements of the EPC, especially with regard to novelty, inventive step, clarity, disclosure in the documents as filed and unity (Arts. 54(1) and (2), 56, 84, 123(2) and 82 EPC).
10. In your reply you should also identify the difference between the new claims and the state of the art and its significance, and present the invention in such a way that both the technical problem to be solved vis-à-vis the state of the art and the solution found (see Rule 27(1)(c) EPC and Guidelines C-IV, 9.5), as well as your position on the question of inventive step, can be understood.
11. According to the Guidelines (C-III, 4.4) an independent claim should specify clearly all the essential features needed to define the invention, i.e. each independent claim must indicate all the features necessary to solve the problem on which the invention is based.
12. Your attention is drawn to the fact that the application may not be amended in such a way that its subject-matter extends beyond the content of the application as filed (Art. 123(2) EPC). Therefore, and also in view of the Guidelines E-II, 1 and C-VI, 5.4, you should explain from where in the original application documents the new features in any newly formulated claims have been directly and unambiguously derived.

DOCUMENT I (State of the Art)

(This document is identical with Document I in Paper A)

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
5 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
10 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
15 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
20 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
25 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 parent structure prior to oxyethylation by adding propylene oxide. Furthermore, oxyalkylation can be performed 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)

(This document is identical with Document II of Paper A)

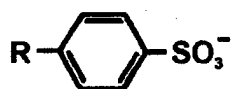
6.2 Sulphonates

Sulphonates are salts of sulphonic acids, in which a hydroxysulphonyl group ($-\text{SO}_3\text{H}$) 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 $\text{p-R-C}_6\text{H}_4\text{-SO}_3^-$ 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 detergents and cleansing agents, dodecylbenzene sulphonates are nowadays the most important group of synthetic tensides in terms of quantity.

- 5 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
15 leaded, mixing vessels, since the reaction mixture is highly corrosive. The reaction is described below using dodecylbenzene as an example:



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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
25 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
30 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.

DOCUMENT III (State of the Art)

We have found a new class of emulsifiers which opens up completely new perspectives for many fields of activity. Hitherto, anionic emulsifiers have often been combined with nonionic emulsifiers, for example, to avoid, to a major extent, the disadvantages of each type of emulsifiers.

- 5 Known anionic emulsifiers are alkylhydroxybenzene sulphonates or alkylbenzene sulphonates having the schematic formula $\text{R-C}_6\text{H}_3(\text{X})\text{-SO}_3^- \text{M}^+$ (wherein $\text{X} = \text{-OH}$ or -H) which can easily be obtained by sulphonating benzenes substituted by alkyl (R) and, optionally, hydroxy groups with concentrated or fuming sulphuric acid or sulphur trioxide. Emulsions stabilised by these emulsifiers, are however, as is known, very sensitive to salts or other electrolytes. This makes them unsuitable for the
10 production of emulsions which should be stable to the addition or effect of electrolytes (salts).

Nonionic emulsifiers do not have this sensitivity to salts, but their emulsifying strength and the resulting emulsion stability are highly dependent on temperature. Their cloud points which usually lie within the range of temperatures normally used, e.g. up to 80°C , represent a particular disadvantage.

15

Our new products combine the advantageous properties of both classes of emulsifiers, whilst avoiding most of their disadvantages, particularly electrolyte sensitivity and the narrow range of applicable temperatures.

- 20 The new emulsifiers have a hydrophobic parent structure, namely the alkyl benzene moiety of which the alkyl group normally has 6 to 16 carbon atoms, although longer chains of up to about 24 carbon atoms have in many cases shown themselves to be still suitable. To this moiety is bonded a hydrophilic moiety present as a sulphonated polyoxyethylene chain. The compounds can be described by the formula $\text{R-C}_6\text{H}_4\text{-(O-C}_2\text{H}_4\text{R')}_n\text{-O-SO}_3^- \text{M}^+$, wherein R is the alkyl group described above, R'
25 hydrogen, M^+ a cation which neutralises the terminal sulphate group and, in general, represents an

alkali metal ion or ammonium; n is usually within the range of 1 to 15, often up to 10 but in some cases 4 or less. The two substituents are usually bonded in the 1- and 4-positions of the benzene ring (para-position).

- 5 The emulsifiers are prepared very simply by oxyalkylating an alkyl phenol, e.g. 1-hydroxy-4-dodecylbenzene, at temperatures of 100 to 150°C, the molar ratio of the ethylene oxide to the alkyl phenol being 2 to 10. The ethylene oxide is normally added at only slightly increased pressure (up to about 0.6 MPa). The 1-hydroxy-4-dodecylbenzene is commercially available as dodecylphenol, either as a pure compound or an homologous mixture of alkyl phenols, their alkyl
10 groups having about 10 to 14 carbon atoms, the average being 12. Other suitable alkyl phenols, normally in their para-form and with the abovementioned chain lengths, are also commercially available.

- The terminal hydroxy group of the reaction product $R-C_6H_4-(O-C_2H_4R')_n-OH$ is then converted to
15 a sulphate group by reaction with the sulphonating agent, such as concentrated or fuming sulphuric acid or gaseous or dissolved sulphur trioxide (mostly diluted with an inert gas), and then immediately neutralised. The sulphonation may, for example, be carried out using directly a ca. 4 to 8% by volume sulphur trioxide/air mixture obtainable by the combustion of sulphur and subsequent contact process. Since these are simple, basic reactions with which a chemist is familiar, they do not need to
20 be described in detail here. It should however be pointed out that during sulphonation the temperature should not exceed about 80°C and after sulphonation and neutralisation it should not exceed about 120°C. In unfavourable circumstances (such as heating under acidic conditions) the sulphate can get split off which leads to the desired advantageous properties being lost. Temperatures of 30 to 50°C are usually sufficient for sulphonation. The oxyalkylation is not critical
25 in this respect, so temperatures of up to 130 or even 150°C do not present a problem.

- An additional means of influencing the properties is to replace part of the oxyethyl groups with oxypropyl and/or oxybutyl groups. The oxyalkylation is then not carried out with pure ethylene oxide but with mixtures of this compound with propylene oxide and/or butylene oxide, or else the
30 ethylene oxide is replaced in the course of the reaction with the other compounds mentioned. In the

case of propylene oxide and butylene oxide $R' = \text{methyl or ethyl}$. A typical variation of this kind is, for example, to add 2 propylene oxide units to 4 ethylene oxide units. The reaction conditions remain practically the same in this case.

5 Example 1

One mole (220,4 g) of para-nonyl phenol were dissolved in 1 l of xylene and charged to a stirred autoclave under nitrogen as protective gas. After heating to 120°C, 4 moles (160 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
10 until the pressure had dropped to 0.11 MPa. The product was flushed with nitrogen and then reacted with sulphur trioxide (about 5% by vol. of SO_3 and about 95% by vol. of nitrogen) at a temperature of 35°C in a glass reactor with intensive stirring until an amount of 84 g (1.05 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
15 largely removed by distilling off the azeotrope xylene/water.

The product had an acid number of 117.6, i.e. one acid group was present per molecule, the formula being $p\text{-C}_9\text{H}_{19}\text{-C}_6\text{H}_4\text{-(O-C}_2\text{H}_4\text{)}_4\text{-OSO}_3\text{ Na}^+$. Similarly, para-dodecylphenol, likewise commercially available, could also be reacted in the same way. Both emulsifiers are highly suitable for emulsion
20 polymerisation or microsuspension polymerisation of vinyl acetate, of vinyl chloride and of styrene.

Example 2

10g sodium-4-[ω -sulphato-tetra(ethyleneoxy)]-1-dodecyl benzene (see Example 1) were mixed with
25 250g of ethylene glycol dioleate, a conventional textile lubricant, and the mixture was used as lubricant in the production of polyester fibres.

The versatility of our emulsifiers is also apparent from the fact that they can be used for all the applications in which sulphonated benzene derivatives have been used hitherto: in hair shampoo and
30 as emulsifying agent for simpler production of colloidal metal powder dispersions. Other areas in

which they could be used are in drilling fluids for deepwell drilling in oil recovery, for example, and as an additive in the field of concrete construction. The water-cement ratio can then be diminished, thereby improving both the concrete's workability and strength. Moreover, like most other emulsifiers based on sulphonated benzene derivatives, our emulsifiers act as air-entraining agents.

- 5 For all these applications, the concentration of the emulsifier is in the range of 0.1 to 10% by weight. Frequently, the amounts used are 1 or 2 to 5 or 6% by weight. The optimum amount can be ascertained by carrying out a few simple optimisation tests familiar to the skilled person.

Aromatic compounds can be sulphonated without difficulty using sulphur trioxide. The hitherto usual sulphonating agent, sulphuric acid, which is employed as concentrated or even fuming sulphuric acid (oleum), has always entailed several serious disadvantages which can be avoided by using SO_3 .

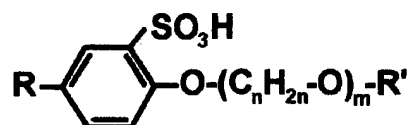
- 5 Sulphuric acid is prepared from sulphur trioxide and water; it has a strong corrosive effect and is therefore associated with risks to the staff handling it. The apparatus also has to be suitably designed, for example by lining the surfaces coming into contact with the acid with lead, which is not very resistant mechanically.
- 10 When sulphuric acid is used for the sulphonation reaction under consideration here, water is also formed which quickly brings the concentration into a range in which the reaction comes to a halt. Furthermore, sulphonation with sulphuric acid gives rise to mostly dark-coloured products, which indicate the presence of decomposition products.
- 15 Sulphur trioxide, on the other hand, is added to the aromatic compounds without water being split off. The products are usually only slightly discoloured, that is, they contain fewer impurities (decomposition products).

- Sulphur trioxide is prepared by combustion of elementary sulphur in the so-called contact process. In
- 20 this process, it is usually obtained in diluted form and is immediately ready for further use.

- Sulphonation with SO_3 is usually carried out at moderate temperatures of up to about 125°C . The higher the temperature, the faster the reaction proceeds, but also the more secondary or even decomposition reactions occur. During the reaction, the aromatic ring is mainly substituted once.
- 25 The production of benzene sulphonic acid from benzene can be cited as an example here. In the case of aromatic compounds already substituted, e.g. toluene, the products obtained are almost exclusively ortho- or para-toluene sulphonic acid, and when 4-dodecyl phenol is used, the product is 2-hydroxy-5-dodecyl benzene sulphonic acid. The product can usefully be employed afterwards as an ammonium or alkali metal salt. Neutralisation is preferably performed in a solvent such as xylene
 - 30 which can form a distillable azeotrope with the water formed in the reaction.

DOCUMENT V (State of the Art)

- The addition of compounds such as lignin sulphonic acids or lignin sulphonates to concrete mixtures is a known method of improving resistance to frost. The water-cement ratio and the amount of fine additives (aggregate) can thereby be reduced, workability is improved through the liquefying effect and concrete quality is increased. The emulsifying effect of the compounds causes the formation of so-called air pores as a result of which the capillary effect of the normally unavoidable concrete pores is substantially reduced or prevented. The concrete cannot then fully soak up water and as temperatures drop to freezing point or below the explosive effect of freezing water in water-filled concrete pores is then virtually or entirely prevented.
- 10 Our sulphonic acid derivatives as described below are also highly suitable for the same purposes. They can usually even be used in smaller quantities than the known products referred to above, or else their effectiveness is increased considerably if used in the same quantities. Moreover, our products have proved to be highly suitable as lubricants in the textile, thread and yarn industries.
- 15 Our products can be described by the following structural formula:



- wherein $\text{R} = \text{C}_{18}$ - to C_{24} - alkyl, in particular stearyl (C_{18}) and behenyl (C_{22}), $n = 2, 3$ or 4 , $m = 2 - 10$, in particular $2 - 4$, $\text{R}' = -\text{CH}_3$, $-\text{C}_2\text{H}_5$ or usually $-\text{H}$. The compounds are present either as free acids (as represented in the formula) or as alkali metal salts (as obtained from the sulphonation according to **Documents II** or **IV** and the subsequent oxyalkylation according to **Document I**).
- 20

- The colourless or slightly yellow products are added to the concrete mixture in amounts of 0.1 to 10% by weight. In typical mixtures for concrete structures which will subsequently be directly exposed to damp, the amount added is 2 to 5% by weight. In the case of applications not so exposed
- 25

to water, 1 to 2% by weight will normally suffice. Further details of the production of concrete mixtures are not necessary since the recipes usually employed can be used. The water is added in accordance with the processing conditions and flowability requirements.

- 5 In the field of textiles and the production of thread and yarn, the effectiveness of the usual lubricants can be considerably improved by our products in terms of lubricity (including a reduction in abrasion on the normal metal tools), antistatic effect and winding properties. This applies in particular where requirements are more stringent because of fast thread speeds. In that case, our sulphonates are added to the usual lubricants in amounts of 1 to 10% by weight, although normally 2 to 5% by
- 10 weight will suffice.