

## Candidate's Answer Paper

Emulsifiers obtainable from substituted benzene, process for the production thereof and use thereof.

The present invention relates to emulsifiers obtainable from substituted benzene by a oxyalkylation and a sulphonation process, a process for the preparation thereof as well as use of the emulsifiers.

### PRIOR ART

From Document I it is known to oxyalkylate among other groups, phenols condensated with hydrophilic poly- or oligoglycol ether. The solubility of the nonionic tensides are influenced by the degree of oxyethylation.

From Document II it is known to use sulphonates, including p-alkyl-benzene sulphonates as emulsifiers.

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-**R-C<sub>6</sub>H<sub>4</sub>-OH**) also known as 1-hydroxy-4-alkyl benzenes. A wide range of products can be manufactured from these **starting materials**, said products differing, in water-solubility, in compatibility with water hardness, in compatibility with basic and acidic media (pH) and in compatibility with salt water.

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.

The emulsifiers are obtainable by a process where they undergo two different and independent reactions, ie. with alkylene oxides (oxyalkylation) on the one hand and with SO<sub>3</sub> (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 be verified by means of titration of the product obtained.

Purely for reasons of simplicity, (i) the starting compound, ie. 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 **R<sup>1</sup>O** wherein **R<sup>1</sup>=-CH<sub>2</sub>-CHR<sup>2</sup>-** and **R<sup>2</sup>=-H, -CH<sub>3</sub> and -CH<sub>2</sub>H<sub>5</sub>**, 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 known as such to the expert, see **Document 1**. 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. Sulphuration of organic compounds is generally known to the expert, see **Document II**. For this reason only a few decisive features will be discussed here.

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.

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 presence of electrolytes.

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.

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  $120^{\circ}\text{C}$ . This could also cause the above-mentioned decrease in yield at high temperatures.

The process for producing the emulsifier is as described 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  $\text{SO}_3$  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.

$\text{SO}_3$  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  $\text{SO}_3$  to each benzene ring. Titration of the products has confirmed that the reaction always yields compounds having one acid group per molecule.

The use of  $\text{SO}_3$  provides products with little or no 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  $60^{\circ}\text{C}$  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  $50^{\circ}\text{C}$  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 discoloration in a process in which the reaction is easier to control.

It is possible to produce either completely water-soluble or completely oil-soluble emulsifiers or those with a solubility lying somewhere in between. 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.

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 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 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 10l 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 SO<sub>3</sub> 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 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 <sub>2</sub> solution
			Type	No. of units	
<b>a</b>	8	1	<b>EO</b>	4	+
<b>b</b>	12	1	<b>EO</b>	4	+
<b>c</b>	8	1	<b>EO/PO</b>	4/2	+
<b>d</b>	12	1	<b>EO/PO</b>	4/2	+
<b>e</b>	8	2	<b>EO</b>	4	+
<b>f</b>	12	2	<b>EO</b>	4	+
<b>g</b>	18	2	<b>EO</b>	4	+
<b>h</b>	18	1	<b>EO</b>	4	+
<b>i*</b>	12	-	-	0	-

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

## CLAIMS

1. An emulsifier consisting of compounds having one anionic group obtainable by a process starting from substituted benzene having the formula



wherein R is an alkyl group having 6 to 24 carbon atoms,

subjecting the substituted benzene to oxyalkylation before or after a sulphonation reaction,

said oxyalkylation is carried out by reacting the substituted benzene with an alkylene oxide of the formula  $\text{R}^1\text{O}$ , wherein  $\text{R}^1 = \text{-CH}_2\text{-CH R}^2$

and  $\text{R}^2 = \text{-H, -CH}_3$  and  $\text{-C}_2\text{H}_5$  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, and the degree of oxyalkylation  $n$  being from 1 to 10, and the sulphonation is carried out by adding a sulphonating agent, intensively mixing and effectively cooling the mixture, not allowing the reaction temperature to exceed 135°C,

directly after sulphonation, neutralising the sulphonated reaction product,

optionally followed by a drying stage.

2. An emulsifier according to claim 1, which is a mixture of homologous compounds made from the same starting materials, the chain length of R and the degree of oxyalkylation  $n$  varying around an average value.
3. An emulsifier according to any of the preceding claims, wherein R is a linear alkyl group having 8 to 16 carbon atoms.
4. An emulsifier according to claim 2, wherein the average value of chain length of R is 10 to 14.
5. An emulsifier according to claim 2 or claim 4, wherein the average value of  $n$  ranges from 2 to 4.
6. An emulsifier according to any of the preceding claims, wherein the sulphonation is carried out before the oxyalkylation.
7. An emulsifier according to claim 6, wherein R is 8 and  $n$  is 4.
8. An emulsifier according to claim 6, wherein R is 12 and  $n$  is 4.
9. An emulsifier according to claim 6, wherein R is 18 and  $n$  is 4.
10. An emulsifier according to claim 6, wherein the average number of C-atoms in the alkyl group R is 12 and the average value of  $n$  is 4.
11. An emulsifier according to any of the preceding claims, wherein the sulphonating agent is  $\text{SO}_3$ .

12. A process of producing an emulsifier as defined in any of claims 1 to 11.
13. A process according to claim 12, wherein  $\text{SO}_3$  as the sulphonating agent is used in a form diluted with a carrier gas to a concentration of 4 to 8% by volume, and 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  $\text{SO}_3$  to each benzene ring.
14. A process according to claim 12 or 13, wherein the reaction temperature is up to  $80^\circ\text{C}$ .
15. A process according to claim 14, wherein the oxyalkylation is carried out before the sulphonation.
16. Use of an emulsifier according to any of claims 1 to 11 or produced according to any of claims 12 to 14.
17. Use according to claim 16 as a lubricant in the polymer fibre and yarn industry.
18. Use according to claim 16 as an additive to concrete.
19. Use according to claim 16 as an additive to an aqueous medium in secondary or tertiary oil recovery.

#### Notes

File another application directed to a sulphonation process using  $\text{SO}_3$  as the sulphonation agent.