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Description

This invention relates to overbased additives containing sodium sulphonate.

Lubricants often need the presence of detergents and there is an increasing need for detergent additives which have high basicity, especially automotive lubricants where their high basicity neutralises acids formed during operation of the engine. This invention relates to such high basicity or "overbased" additives which contain colloiddally dispersed carbonates and include the presence of sodium sulphonate.

Various patents disclose processes for making overbased additives including those containing sodium sulphonates such as US 3489682, US4326972 and GB1481553 but few teach the necessity of using an alkoxyalkanol or of hydrolysing after the addition of carbon dioxide. Examples of prior art processes are found in GB1388021, GB1551820, GB2055885, GB2055886, US5346493, US3428561, US3437465, US3471403, and US3488284 which include references to alkoxide formation or the use of alkoxyalcohols in preparing overbased additives. Prior art processes tend to form sodium sulphonate products which are hazy due to instability of the colloid. We have surprisingly found that a careful balance of water in relation to the amount of sodium hydroxide used, which was not appreciated by the prior art, provides an excellent route to overbased sodium sulphonate suitable as fuel or lubricant additives.

In accordance with this invention, an oil solution of a highly basic sodium sulphonate is prepared by a process which comprises:

- (a) heating sodium hydroxide with an alkoxyalkanol and a solvent to remove as an azeotrope with said alkoxyalkanol and solvent a controlled amount of water formed in the reaction of a part of the sodium hydroxide with the alkoxyalkanol so as to form a mixture comprising unreacted sodium hydroxide and sodium alkoxyalkoxide
- (b) adding to the mixture an organic sulphonic acid so as to react with a part of basic sodium compounds therein and form the sodium salt of the sulphonic acid and water;
- (c) thereafter introducing carbon dioxide into the reaction mixture so as to react with the basic sodium compounds therein;
- (d) removing solvent by distillation; and
- (e) adding base oil to the process during one of steps (b), (c) and (d) so that the desired product is obtained, in which the amount of sodium alkoxyalkoxide produced in step (a) is controlled by azeotropic removal of water in that step such that the amount of water produced in step (b) and (c) is not greater than the amount stoichiometrically required to hydrolyse the alkoxide produced in step (a).

Thus, in the process of the invention in the case when the alkoxyalkanol and sulphonic acid are the only species present capable of reacting with sodium hydroxide to form water in steps (a) and (b) the azeotrope is removed in step (a) until the sum of number of moles of sodium hydroxide in excess of that reacted in step (a) plus the number of moles of organic sulphonic acid to be added to step (b) is not more than the number of moles of sodium hydroxide reacted in step (a). That is, $A + C \leq B$ (wherein A is the number of moles of sodium hydroxide in excess of that reacted with alkoxyalkanol in step (a), B is the number of moles of sodium hydroxide reacted with alkoxyalkanol in step (a) and C is the number of moles of sulphonic acid added in step (b)). In the case where $A + C < B$ and sufficient water is not formed to hydrolyse the formed sodium alkoxyalkoxide, then more water, preferably as an alkoxyalkanol/water mixture, is added after step (c) and before step (d) to hydrolyse any remaining alkoxyalkoxide.

As discussed in more detail hereinafter additional reactants, such as further surfactants may be added to the process, and in the event that these additional reactants are capable of reacting with sodium hydroxide to form water the azeotrope may be carried further to form more alkoxide provided that :

$$A + C + \sum_n 2nD_n \leq B$$

where D_n is the number of moles of additional reactant of which 1 mole is capable of reacting with sodium hydroxide to form n moles of water in excess of the amount of water produced if that sodium hydroxide were carbonated. Thus $n = y-x/2$ where x moles of sodium hydroxide react with one mole of the additional reactant to produce y moles of water. As indicated where more than one reactant is present the product $2n.D_n$ is summed for all the reactants, thus

$$A + C + (2y_1-x_1) D_1 + (2y_2-x_2) D_2 + \dots \leq B$$

where there are D_1 moles of the first reactant of which one mole reacts with x_1 moles of sodium hydroxide to produce y_1 moles of water, D_2 moles of a second reactant of which one mole reacts with x_2 moles of sodium

hydroxide to produce y_2 moles of water, and so on.

This process enables one to obtain highly basic sodium sulphonates having relatively high total base numbers (TBN) of at least 250 mg KOH/g. TBN is a measure of basicity of a product and is measured by the method laid down in ASTM D2896.

5 One of the starting materials is sodium hydroxide and the normal commercial grade can be used.

The solvent can be, for example, any aliphatic, naphthenic or aromatic solvent provided it forms an azeotrope with water; in particular, n-hexane, n-heptane, n-octane, n-dodecane, benzene, xylene, toluene, white spirit, naphtha or isoparaffins.

10 Usually, it is a hydrocarbon solvent but it could be a halogenated hydrocarbon, e.g. chlorobenzene. The most preferred solvents are toluene and xylene.

Although aromatic substituted alkoxyalkanols, could be used, it is preferable to use an aliphatic alkoxyalcohol, especially those containing 2 to 10 carbon atoms per molecule. Suitable examples of aliphatic alkoxyalcohols are methoxy methanol, methoxy ethanol, methoxy isopropanol, ethoxy methanol, 2-ethoxy ethanol, 2-butoxy-ethanol or propylene glycol ethers, e.g. methoxy propanols, butoxy propanols or phenoxy propanols.

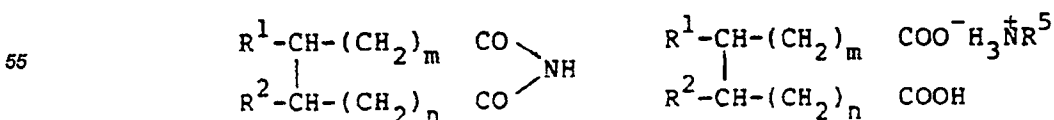
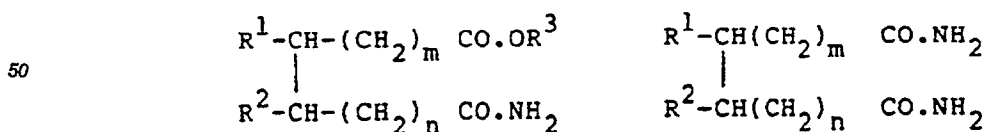
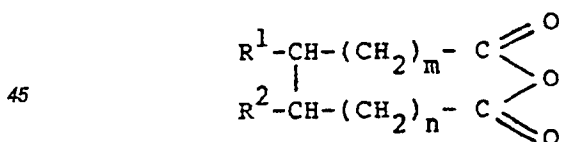
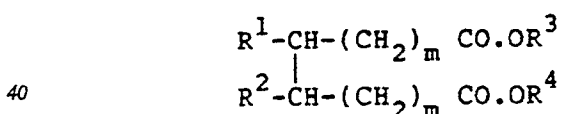
15 The amount of alkoxyalcohol employed in the process per mole of sodium hydroxide will usually be in the range of 0.5 to 50, preferably 0.75 to 2.

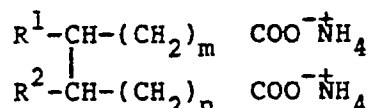
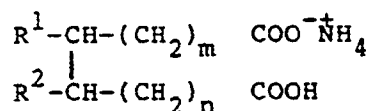
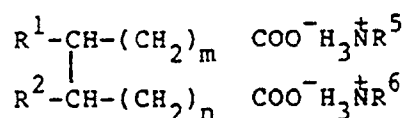
The organic sulphonic acids are usually obtained from the sulphonation of natural hydrocarbons or synthetic hydrocarbons; e.g. a mahogany or petroleum alkyl sulphonic acid; an alkyl sulphonic acid or an alkaryl sulphonic acid. Such sulphonic acids are obtained by treating lubricating oil basestocks with concentrated or fuming sulphuric acid to produce oil-soluble "mahogany" acids or by sulphonating alkylated aromatic hydrocarbons. Sulphonates derived from synthetic hydrocarbons include those prepared by the alkylation of aromatic hydrocarbons with olefins or olefin polymers; e.g. C_{15} - C_{30} polypropenes or polybutenes. Also suitable are the sulphonic acids of alkyl benzenes, alkyl toluenes or alkyl xylenes, which may have one or more alkyl groups wherein each group, which may be straight or branched, preferably contains at least 12 carbon atoms. The preferred sulphonic acids have molecular weights of from 300 to 1000, for example, between 400 and 800, e.g. about 500. Mixture of these sulphonic acids may also be used.

25 The mole ratio of sulphonic acid to sodium hydroxide is usually between 1:5 and 1:36, preferably 1:10 to 1:25.

Although a sulphonic acid, e.g. an alkyl benzene sulphonic acid, may be sufficient to act as the surfactant for the overbased material of the invention, especially when it has a relatively high molecular weight aliphatic chain e.g. of molecular weight more than about 400, very often it is desirable to include another surfactant having a long aliphatic chain usually with a molecular weight of 700 or greater, for example about 900, in the reaction mixture.

35 This additional surfactant is a dicarboxylic acid or anhydride, or an ester, amide imide, amine salt or ammonium salt of a dicarboxylic acid and as such include those represented by the formulae:





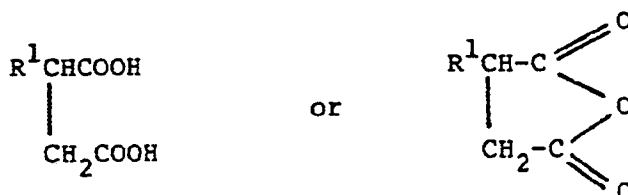
where R¹ and R² are hydrogen or optionally-substituted hydrocarbyl groups of at least 30 carbon atoms provided they are not both hydrogen, m and n are zero or integers, R³ and R⁴ are hydrogen or hydrocarbyl groups and R⁵ and R⁶ are hydrocarbyl groups.

It is preferred that R² be hydrogen and that m and n be zero or a small integer, e.g. 1 or 2. In general, acids or anhydrides are the preferred surfactant. However, if an ester, monoamide or ammonium salt is used, it is preferred that R³, R⁴, R⁵ and R⁶ are alkyl groups, especially a C₁ to C₅ alkyl group, for example, methyl, ethyl or propyl. If desired, however, the ester could be derived from a glycol, in which case R³ and R⁴ would not be separate hydrocarbyl groups, but instead, the residue of a glycol, for example, ethylene glycol or propylene glycol.

The most preferred compounds are those where R¹ contains 40 to 200 carbon atoms and where R¹ has no atoms other than carbon, hydrogen and halogen, and especially when it only contains carbon and hydrogen atoms, i.e., it is a hydrocarbyl group. Preferred hydrocarbyl groups are aliphatic groups.

The acid, anhydride, ester, amide, imide, amine salt or ammonium salt is preferably substantially saturated, but the substituent group, for example, the group R¹, may be unsaturated. In practice, it is preferred that the substituent group be a polymer of a monolefin, for example, a C₂ to C₅ monolefin, such as polyethylene, polypropylene or polyisobutene. Such polymers will usually have only one double bond so that they could be regarded as predominantly saturated, especially since they must have at least 30 carbon atoms.

The most preferred acid or anhydride is one of the formula:



especially where R¹ is polyisobutenyl, i.e. a polyisobutenyl succinic acid or anhydride, preferably where R¹ has 30 to 200 carbon atoms, especially 45 to 60 carbon atoms. Such anhydrides are frequently known as PIBSA.

When such an acid, anhydride or ester is used, the molar ratio of organic sulphonic acid to the acid, amide, imide, amine salt, ammonium salt, anhydride or ester can vary but is usually between 20:1 and 2:1, e.g. between 15:1 and 4:1.

The first step of the process is the addition of sodium hydroxide to the mixture of alkoxyalkanol and solvent and reaction of a part of the sodium hydroxide to form the sodium alkoxyalkoxide. The reaction mixture is heated so that the temperature is slowly increased and the water formed by the reaction to form sodium alkoxyalkoxide is removed as an azeotrope with the solvent and the alkoxyalkanol. Little solvent is normally removed in the azeotrope, and the reaction vessel may be equipped with a condenser so that substantially all solvent is returned to the reaction vessel. The recovered azeotrope then comprises water and alkoxyalkanol with substantially no solvent. This heating which in effect is azeotropic distillation effectively controls the amount of sodium hydroxide converted to alkoxyalkoxide since the removal of water drives the alkoxyalkoxide-forming reaction. The extent to which this reaction is driven and formed water is removed is critical since surprisingly it has been found that excess water in the system tends to result in a hazy and unsatisfactory product. It has further been discovered that a surprising and effective means of preventing this haze formation is by using the alkoxyalkoxide

formation and subsequent hydrolysis as a control of the water in the system. By forming alkoxyalkoxide in such an amount that the water required to hydrolyse it is at least equal to the water generated in the remaining steps of the process, effective control over haze may be obtained.

Usually the azeotropic distillation takes at least an hour, and times of from 1.5 to 2 hours are typical for small scale operations.

In the next step the organic sulphonic acid and optionally the dicarboxylic acid, anhydride or ester, amide, imide, amine salt or ammonium salt are added preferably at 50°C to 70°C to the reaction mixture which may then be heat-soaked, e.g. at a temperature of about 80°C to 100°C. The sulphonic acid and dicarboxylic acid, anhydride, ester, amide, imine, amine salt or ammonium salt are usually introduced as solutions in diluent oil, e.g. an aliphatic or aromatic hydrocarbon. The purpose of this heat soaking is to effect neutralisation of the organic sulphonic acid, and if used, the dicarboxylic acid, anhydride, monoamine salt or monoammonium salt by the sodium hydroxide. The time taken for this heat soaking is usually from 10 to 30 minutes, e.g. about 20 minutes.

The amount of sodium hydroxide and organic sulphonic acid are related and dependent on the degree of reaction with alkoxyalkanol in step (a) as discussed above. A part of the sodium hydroxide reacts with the alkoxyalkanol according to the equation



(where R is an alkoxyalkyl group). B moles of sodium hydroxide react with alkoxyalkanol in step (a) in this and B moles of water are formed and removed as azeotrope, while there is an excess of A moles of sodium hydroxide unreacted in step (a). If C moles of organic sulphonic acid are introduced in step (b) to react with a further part of the sodium hydroxide then C moles of water are formed and $A + C \leq B$ to ensure that excess water is not formed which would give rise to haze. The reaction of sulphonic acids with sodium hydroxide may be represented:

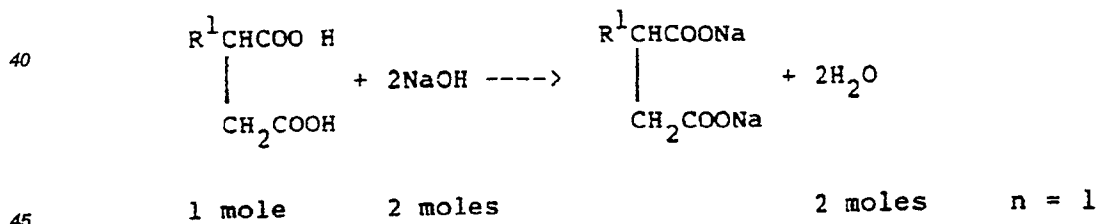


(where R'' is the organic group of the sulphonic acid). If a further surfactant is used, such as dicarboxylic acid or anhydride which also reacts with sodium hydroxide to form water than an appropriate adjustment must be made such that

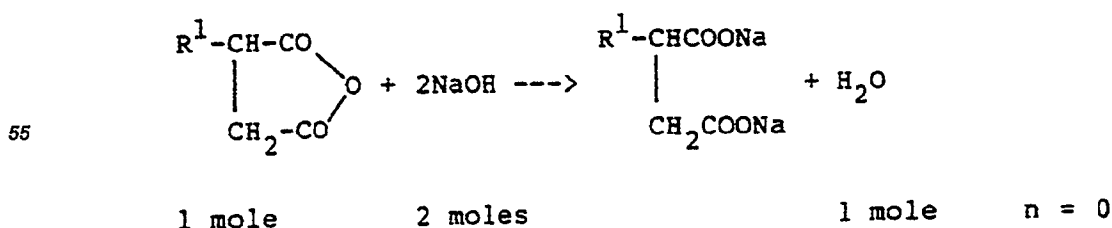
$$A + C + \sum_n 2n \cdot D_n \leq B$$

Thus, if a dicarboxylic acid or a mono-amine or mono-ammonium salt of a dicarboxylic acid is employed as surfactant (where 1 mole of the surfactant reacts with 2 moles of sodium hydroxide to form 2 moles of water in total or 1 mole in excess of the 1 mole of water formed by carbonating 2 moles of sodium hydroxide) then $n = 1$ and $A + C + 2D_2 \leq B$ where D_2 is the number of moles of dicarboxylic acid, mono-amine or salt.

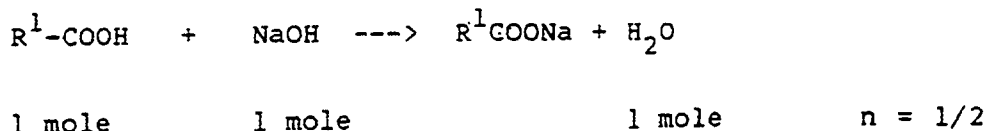
Thus:



If a dicarboxylic acid anhydride is used (where 1 mole of anhydride reacts with 2 moles of sodium hydroxide to form only one mole of water and thus no excess of water) then $n = 0$ and $A + C \leq B$, that is independent of the number of moles (D_0) of the anhydride present. Thus:



If a monocarboxylic acid were used as surfactant (where 1 mole of acid reacts with only 1 mole of sodium hydroxide to form 1 mole of water, the excess is 1/2 mole of water) $n = 1/2$ and $A + C + D_1 \leq 0$ where D_1 moles of the monocarboxylic acid are present. Thus:



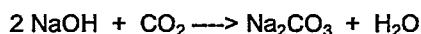
It is preferred that: $A + C + \sum 2n.D_n = B$

since the step of adding additional water to the carbonated reaction mixture is then unnecessary.

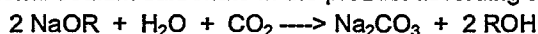
After this heat soaking step, carbon dioxide is introduced to react with the basic sodium compounds in the reaction mixture which is preferably maintained at a temperature from ambient to the reflux temperature of the mixture, typically 120°C, more preferably between 80°C and 100°C, for example, about 90°C. The preferred amount of carbon dioxide which is blown into or injected into the reaction mixture is 90% to 115%, e.g. about 105% of the theoretical amount required to react with available basic sodium compounds.

In practice, carbon dioxide is blown in until no more carbon dioxide is absorbed, e.g. when the gas inlet and exit rates, as measured on gas rotameters are the same. Rates are usually chosen to introduce the carbon dioxide over 2 to 4 hours, e.g. about 3 hours.

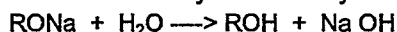
The basic sodium compounds which will react with the carbon dioxide include the previously unreacted sodium hydroxide which will react:



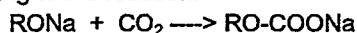
to form the desired overbased product. In addition sodium alkoxyalkoxide formed in step (a) will be hydrolysed and carbonated to form additional sodium carbonate in the product according to the overall reaction:



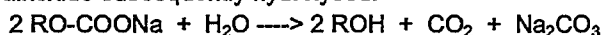
in which the water for the hydrolysis (on the left hand side of the reaction) is obtained from the reaction of sulphonic acid with sodium hydroxide, the reaction of carbon dioxide with sodium hydroxide and, if present, the reaction of additional materials such as further surfactants with sodium hydroxide. This overall carbonation and hydrolysis may take place in stages. Either the alkoxyalkoxide may be first hydrolysed:



for example in step (b) and then the formed sodium hydroxide subsequently carbonated, or the alkoxyalkoxide may be carbonated in step (c) according to the reaction:



and the carbonated alkoxyalkoxide subsequently hydrolysed:



or a combination of these steps may take place giving the overall reaction set out above. In the case where $A + C + \sum 2n.D_n < B$ in a subsequent step water may be added, preferably as a mixture of water and alkoxyalkanol, to convert the residual carbonated sodium alkoxyalkoxide to sodium carbonate.

Water or any mixture of water and alkoxyalkanol can be used preferably between 1:6 and 1:2 water:alkoxyalkanol (by weight). The water/alkoxyalkanol mixture is usually slowly added to the reaction mixture to convert the residual carbonated sodium alkoxyalkoxide to sodium carbonate, alkoxyalkanol and carbon dioxide and this addition continues until the evolution of carbon dioxide ceases.

The next step in the process is to remove the alkoxyalkanol and solvent by distillation. Usually, this takes place by atmospheric distillation typically at a temperature of about 180°C, optionally followed by distillation under reduced pressure whence the residual solvent and alkoxyalkanol will be removed.

Following this distillation step, solid contaminants may be removed from the product preferably by filtration or centrifuging. The desired product is the filtrate or centrifugate.

The desired product is a solution in oil and therefore base oil is added to the process in step (b), (c) or (d). Most preferably the oil is added with the sulphonic acid in step (b). Base oils used in the process are preferably lubricating oils as described hereinafter.

The process of the invention enables a high quality, high TBN sodium sulphonate product to be obtained in good yields (e.g. 95% + of theoretical) with reduced amounts of material losses in sludge and/or sediment and reduced problems in waste disposal which can arise when large amounts of sludge or flocculent material are produced. The process of the invention in particular provides a means of preparing a preferred product with a TBN of at least 250, preferably 250 to 600 mg (KOH)/g, more preferably 350 to 500, specifically in the region of 400 mg (KOH)/g.

The overbased additive of this invention is suitable for use in oleaginous compositions such as fuels or

lubricating oils for gasoline or diesel engines, both mineral and synthetic. The lubricating oil may be an animal, vegetable or mineral oil, for example, petroleum oil fractions ranging from naphthas or spindle oil to SAE 30, 40 or 50 lubricating oil grades, castor oil, fish oils or oxidised mineral oil.

5 Suitable synthetic ester lubricating oils include diesters such as dioctyl adipate, dioctyl sebacate, didecyl azelate, tridecyl adipate, didecyl succinate, didecyl glutarate and mixtures thereof. Alternatively the synthetic ester can be a polyester such as that prepared by reacting polyhydric alcohols such as trimethylolpropane and pentaerythritol with monocarboxylic acids such as butyric acid, caproic acid, caprylic acid and pelargonic acid to give the corresponding tri- and tetra-ester.

10 Also, complex esters may be used as base oils such as those formed by esterification reactions between a dicarboxylic acid, a glycol and an alcohol and/or a monocarboxylic acid.

Blends of diesters with minor proportions of one or more thickening agents may also be used as lubricants. Thus one may use blends containing up to 50% by volume of one or more water-insoluble polyoxyalkylene glycols, for example, polyethylene or polypropylene glycol, or mixed oxyethylene/oxypropylene glycol.

15 The amount of overbased detergent added to the lubricating oil should be a minor proportion, e.g. between 0.01% and 10% by weight, preferably between 0.1% and 5% by weight.

The final lubricating oil may contain other additives according to the particular use for the oil. For example, viscosity index improvers such as ethylene-propylene copolymers may be present as may ashless dispersants such as substituted succinic acid based dispersants, other metal containing dispersant additives, well known zinc dialkyldithio-phosphate antiwear additives, antioxidants, demulsifiers, corrosion inhibitors, extreme pressure additives and friction modifiers. In particular, the oils of the invention may contain ashless dispersant, a 20 zinc dialkyl dithiophosphate and copper in an oil soluble form (preferably in an amount of 5 to 500 ppm copper) as antioxidant.

The invention also includes an additive concentrate comprising an oil solution of an overbased sodium sulphate of the invention comprising 10 to 90 wt %, preferably 40 to 60 wt % overbased sodium sulphate 25 (active matter) based on the weight of oil.

When used in fuels as a detergent or combustion improver the overbased material is used in minor proportions, e.g. between 0.01 and 10% by weight of the fuel.

The invention is now described with reference to the following examples:

30 Examples

In these Examples the charge quantities were

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	sodium hydroxide	560 g
5	2-ethoxyethanol	1450 g
	toluene	1200 g
10	a 70% oil solution of mixed alkyl benzene sulphonic acids (the major component being C ₂₄ branched alkyl benzene sulphonic acids)	536 g
15		
20	polyisobutenyl succinic anhydride 1000 MW (PIBSA)	80 g
	mineral diluent oil (Stanco 150)	473 g
25	carbon dioxide	780 cm ³ /min
	water/2-ethoxyethanol	1:4 mixture

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The general procedure was as follows:

1. 2-Ethoxyethanol and toluene were charged to a 5 litre glass reactor fitted with stirrer, thermocouple, Dean and Stark receiver, condenser and nitrogen purge.
2. Sodium hydroxide was added and the temperature slowly increased until azeotropic conditions were attained and water was being steadily removed without losing solvent through the condenser. This condition was continued until the amounts of azeotrope in the attached table were recovered. The azeotrope is predominantly water with 2-ethoxyethanol and minor traces of toluene. Its composition was determined by gas chromatography.
3. On reaching the desired level of water removal (i.e. conversion of NaOH to NaOR) a premixture of sulphonic acid, PIBSA and oil at 60°C was added. The contents of the reactor were then stabilised at 90°C and the Dean and Stark receiver replaced by a simple reflux condenser.
4. Carbon dioxide was then injected into the solution until no further CO₂ was being absorbed. This point was reached when the gas inlet and exit rates, as measured on gas rotameters, were the same. The CO₂ was then turned off.
- 45 5. A 1:4 mixture of water and 2-ethoxyethanol was then slowly added from a dropping funnel to convert any residual carbonated sodium ethoxyethoxide to sodium carbonate, 2-ethoxyethanol and carbon dioxide. When the evolution of CO₂ ceased the water/2-ethoxyethanol addition was stopped and the amount of water added calculated.
6. The apparatus was then changed from reflux to distillation conditions and a nitrogen purge installed. The temperature was then slowly raised to 180°C and residual solvents (2-ethoxyethanol and toluene) removed. At 180°C a vacuum of 20 inches of mercury was applied to remove the last traces of solvent.
7. The product was then filtered through a bed of Dicalite 4200 filter aid in a pressure filter to give the finished product.

55 In these Examples D to L are within the scope of the invention with Examples E to G preferred. Examples A, B and C are for comparison purposes.

Example A

5 No water was removed by azeotropic distillation as described in step 2 above. A mixture of NaOH, 2-ethoxyethanol, toluene, sulphonic acid, PIBSA and oil was carbonated at 90°C. Some CO₂ was absorbed but product gradually hazed as colloid precipitated from solution. The experiment was abandoned.

Example B

10 140 cm² of an azeotrope was recovered in step 2. On carbonation the reaction mixture gradually hazed and on distilling colloid precipitation occurred.

Example C

15 This experiment was carried out on a larger scale and the figures quoted are scaled down to provide a comparison. Water was added at the hydrolysis step but no carbon dioxide was given off - indicating that this was in excess of that required for hydrolysis. The product filtered well but was hazy even after passing through the finest filter aid.

Example D

20 Water was removed to give 58.5% conversion to alkoxide. The finished product was acceptable but with very slight haze appearance.

Examples E-G

25 All very good preparations. The finished products were all clear and bright with extremely good filtration rates. There was little CO₂ loss during hydrolysis.

Examples H-K

30 All acceptable but the longer azeotrope step meant that more water was necessary to hydrolyse the carbonated alkoxyalkoxide resulting in greater loss of CO₂ during hydrolysis and poorer filtration.

Example L

35 This is a repeat of Example H except that only 20 grams of hydrolysis water is used and thus all the carbonated alkoxide was not converted to the carbonate. The product was very viscous and skinned on exposure to air, but Example H shows that by addition of the appropriate amount of water an excellent product may be prepared.

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SODIUM SULPHONATE PREPARATIONS

	A	B	C	D	E	F	G	H	J	K	L
Volume of azeotrope recovered, cm ³	0	140	150	180	186	200	215	220	259	269	220
Amount of water in azeotrope, g	0	115	123	147.5	152.5	164	177	181	212.8	226	181
Amount of alkoxide formed. Based on water removed, g	0	45.6	48.8	58.5	60.6	65.1	70.2	71.8	84.4	89.7	71.8
Water added during hydrolysis step, g	0	0	5	10	20	20	20	35	88.9	89.1	20
Appearance of product	No product colloid precipitated	No product colloid precipitated	Hazy product	Very slight haze	Good clear + bright	Good clear + bright	Clear	Clear	Clear	Clear	Viscous and skinned on exposure to air
Filtration	No product	Blocked filter	Good	Good	Good	Very rapid	Very rapid	Moderate	Moderate	Moderate	Moderate
TBN	-	-	416	402	417	402	402	405	407	405	405

Claims

- 5 1. A process for making an oil solution of overbased sodium sulphonate having a total base number of at least 250mg KOH/g which process comprises
- (a) heating sodium hydroxide with an alkoxyalkanol and a solvent to remove as an azeotrope with said alkoxyalkanol and said solvent a controlled amount of water formed in the reaction of part of the sodium hydroxide with the alkoxyalkanol;
- 10 (b) adding to the mixture an organic sulphonic acid so as to react with a part of the sodium hydroxide and form the sodium salt of the sulphonic acid and water;
- (c) thereafter introducing carbon dioxide into the reaction mixture so as to react with the basic sodium compounds therein;
- (d) removing solvent by distillation; and
- 15 (e) adding base oil to the process during one of steps (b), (c) or (d) so that the desired product is obtained, in which the amount of alkoxide produced in step (a) is controlled by the azeotropic removal of water in that step such that the amount of water produced in step (b) and (c) is not greater than the amount stoichiometrically required to hydrolyse the alkoxide,
2. A process according to claim 1, wherein in step (b) there is also added a dicarboxylic acid or anhydride, ester, amide, imide, amine salt or ammonium salt thereof, to react with a further part of the basic sodium compounds therein.
3. A process as claimed in claim 1, in which the alkoxyalkanol and sulphonic acid are the only reactants added in steps (a) and (b) which are capable of reacting with sodium hydroxide to form water, and in which the azeotropic removal of water in step (a) is conducted so that:
- 25
$$A + C \leq B$$
- where B is the number of moles of sodium hydroxide which are reacted with alkoxyalkanol in step (a), A is the number of moles of sodium hydroxide in excess of B, and C is the number of moles of sulphonic acid added in step (b).
4. A process as claimed in claim 2, in which additional reactants are present which are capable of reacting with sodium hydroxide to form water, and in which the azeotropic removal of water in step (a) is conducted so that:
- 30
$$A + C + \sum_n 2n \cdot D_n \leq B$$
- 35 where D_n is the number of moles of additional reactant of which one mole is capable of reacting with sodium hydroxide to form n moles of water in excess of the amount of water produced if that sodium hydroxide were carbonated.
- 40 5. A process as claimed in claim 4, in which a dicarboxylic acid and/or a mono-amine salt or mono-ammonium salt thereof is added in step (b) and in which the azeotropic removal of water in step (a) is conducted so that:
- $$A + C + 2D_2 \leq B$$
- 45 where D_2 is the number of moles of dicarboxylic acid, mono-amine salt or mono-ammonium salt of dicarboxylic acid.
6. A process according to any one of the preceding claims wherein the solvent is toluene or xylene.
7. A process according to any one of the preceding claims wherein the alkoxyalkanol contains 2 to 10 carbon atoms per molecule.
8. A process according to any one of the preceding claims wherein the sulphonic acid has a molecular weight of between 400 and 800.
- 50 9. A process according to claim 2 wherein the acid or anhydride added in step (b) is a polyisobutenyl succinic acid or anhydride.
10. A lubricating composition comprising a lubricating oil and 0.01% to 10% by weight of the sodium sulphonate prepared by the process claimed in any of claims 1 to 9.
- 55 11. A lubricating composition as claimed in claim 10, which also contains an ashless dispersant, a zinc dialkyl dithiophosphate and 5 to 500 ppm by weight of copper in oil-soluble form.
12. A fuel composition comprising a fuel and a highly basic sodium sulphonate prepared by the process claimed in any of claims 1 to 9.

Patentansprüche

1. Verfahren zur Herstellung einer Öllösung von überbasischem Natriumsulfonat mit einer Gesamtbasezahl von mindestens 250 mg KOH/g, bei dem

- 5 (a) Natriumhydroxid mit einem Alkoxyalkanol und einem Lösungsmittel erhitzt wird, um als ein Azeotrop mit dem Alkoxyalkanol und dem Lösungsmittel eine kontrollierte Menge des sich bei der Reaktion eines Teils des Natriumhydroxids mit dem Alkoxyalkanol bildenden Wassers zu entfernen,
 (b) zu der Mischung eine organische Sulfonsäure gegeben wird, um mit einem Teil des Natriumhydroxids zu reagieren und das Natriumsalz der Sulfonsäure und Wasser zu bilden,
 10 (c) anschließend Kohlendioxid in die Reaktionsmischung eingeleitet wird, um mit den basischen Natriumverbindungen darin zu reagieren,
 (d) Lösungsmittel durch Destillation entfernt wird und
 (e) Basisöl beim verfahren während einer der Stufen (b), (c) oder (d) zugesetzt wird, so daß das gewünschte Produkt erhalten wird,

15 und bei dem die Menge an in Stufe (a) hergestelltem Alkoxid durch die azeotrope Entfernung von Wasser in dieser Stufe in solcher Weise reguliert wird, daß die in Stufe (b) und (c) erzeugte Menge an Wasser nicht größer ist als die stöchiometrisch erforderliche Menge, um das Alkoxid zu hydrolysieren.

2. Verfahren nach Anspruch 1, bei dem in Stufe (b) außerdem eine Dicarbonsäure oder ein Anhydrid, Ester, Amid, Imid, Aminsatz oder Ammoniumsalz davon zugesetzt wird, um mit einem weiteren Teil der basischen Natriumverbindungen darin zu reagieren.

3. Verfahren nach Anspruch 1, bei dem das Alkoxyalkanol und die Sulfonsäure die einzigen in den Stufen (a) und (b) zugesetzten Reaktanten sind, die mit Natriumhydroxid unter Bildung von Wasser reagieren können, und bei dem die azeotrope Entfernung von Wasser in Stufe (a) so durchgeführt wird, daß:

$$A + C \leq B$$

25 ist, wobei B die Zahl der Mole an Natriumhydroxid ist, die mit Alkoxyalkanol in Stufe (a) umgesetzt werden, A die Zahl der Mole an Natriumhydroxid im Überschuß gegenüber B ist und C die Zahl der Mole an in Stufe (b) zugesetzter Sulfonsäure ist.

4. Verfahren nach Anspruch 2, bei dem zusätzliche Reaktanten vorhanden sind, die mit Natriumhydroxid unter Bildung von Wasser reagieren können, und bei dem die azeotrope Entfernung von Wasser in Stufe (a) so durchgeführt wird, daß:

$$A + C + \sum_n 2n \cdot D_n \leq B$$

35 ist, wobei D_n die Zahl der Mole an zusätzlichem Reaktanten ist, von dem ein Mol mit Natriumhydroxid unter Bildung von n Mol Wasser im Überschuß zu der Menge an Wasser reagieren kann, die produziert würde, wenn das Natriumhydroxid carbonisiert wäre.

5. Verfahren nach Anspruch 4, bei dem eine Dicarbonsäure und/oder ein Monoaminsatz oder Monoammoniumsalz davon in Stufe (b) zugesetzt wird und bei dem die azeotrope Entfernung von Wasser in Stufe (a) so durchgeführt wird, daß:

$$A + C + 2D_2 \leq B$$

ist, wobei D_2 die Zahl der Mole an Dicarbonsäure, Monoaminsatz oder Monoammoniumsalz der Dicarbonsäure ist.

6. Verfahren nach einem der vorangehenden Ansprüche, bei dem das Lösungsmittel Toluol oder Xylol ist.

7. Verfahren nach einem der vorangehenden Ansprüche, bei dem das Alkoxyalkanol 2 bis 10 Kohlenstoffatome je Molekül enthält.

8. Verfahren nach einem der vorangehenden Ansprüche, bei dem die Sulfonsäure ein Molekulargewicht zwischen 400 und 800 besitzt.

9. Verfahren nach Anspruch 2, bei dem die in Stufe (b) zugesetzte Säure oder das in Stufe (b) zugesetzte Anhydrid eine Polyisobutenylbernsteinsäure oder ein Polyisobutenylbernsteinsäureanhydrid ist.

10. Schmiermittelzusammensetzung, die ein Schmieröl und 0,01 bis 10 Gew.% des nach dem Verfahren gemäß einem der Ansprüche 1 bis 9 hergestellten Natriumsulfonats enthält.

11. Schmiermittelzusammensetzung nach Anspruch 10, die außerdem ein aschefreies Dispersionsmittel, ein Zinkdialkyldithiophosphat und 5 bis 500 Gew.ppm Kupfer in öllöslicher Form enthält.

12. Brennstoffzusammensetzung, die einen Brennstoff und ein hochbasisches Natriumsulfonat herstellt nach dem Verfahren gemäß einem der Ansprüche 1 bis 9 umfaßt.

Revendications

1. Procédé de production d'une solution dans l'huile d'un sulfonate de sodium rendu surbasique ayant un indice de basicité totale d'au moins 250 mg de KOH/g, procédé qui consiste :

- 5 (a) à chauffer de l'hydroxyde de sodium avec un alkoxyalcanol et un solvant pour éliminer sous forme d'azéotrope avec ledit alkoxyalcanol et ledit solvant une quantité réglée d'eau formée dans la réaction d'une partie de l'hydroxyde de sodium avec l'alkoxyalcanol ;
- (b) à ajouter au mélange un acide sulfonique organique de manière qu'il réagisse avec une partie de l'hydroxyde de sodium et qu'il forme le sel de sodium de l'acide sulfonique et de l'eau ;
- 10 (c) à introduire ensuite de l'anhydride carbonique dans le mélange réactionnel de manière qu'il réagisse avec les composés de sodium basiques qui s'y trouvent ;
- (d) à chasser le solvant par distillation ; et
- (e) à ajouter une huile de base dans le procédé au cours de l'une des étapes (b), (c) ou (d) de manière à obtenir le produit désiré,

15 la quantité d'alcoolate produite dans l'étape (a) étant réglée par l'élimination azéotropique d'eau dans cette étape de manière que la quantité d'eau produite dans l'étape (b) et dans l'étape (c) ne soit pas supérieure à la quantité stoechiométriquement nécessaire pour hydrolyser l'alcoolate.

2. Procédé suivant la revendication 1, dans l'étape (b) duquel on ajoute également un acide dicarboxylique ou un anhydride, un ester, un amide, un imide, un sel d'amine ou un sel d'ammonium de cet acide, afin qu'il réagisse avec une autre partie des composés de sodium basiques qui s'y trouvent.

3. Procédé suivant la revendication 1, dans lequel l'alkoxyalcanol et l'acide sulfonique sont les seuls corps réactionnels ajoutés dans les étapes (a) et (b) qui soient capables de réagir avec l'hydroxyde de sodium pour former de l'eau, et dans lequel l'élimination azéotropique de l'eau dans l'étape (b) est conduite de manière à vérifier la relation :

$$25 \quad A + C \leq B$$

dans laquelle B représente le nombre de moles d'hydroxyde de sodium qui réagissent avec l'alkoxyalcanol dans l'étape (a), A est le nombre de moles d'hydroxyde de sodium en plus de B, et C est le nombre de moles d'acide sulfonique ajoutées dans l'étape (b).

4. Procédé suivant la revendication 2, dans lequel sont présents d'autres corps réactionnels qui sont capables de réagir avec l'hydroxyde de sodium pour former de l'eau, et dans lequel l'élimination azéotropique d'eau dans l'étape (a) est conduite de manière que soit vérifiée la relation :

$$30 \quad A + C + \sum_n 2n \cdot D_n \leq B$$

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dans laquelle D_n représente le nombre de moles de corps réactionnel ajouté dont une mole est capable de réagir avec l'hydroxyde de sodium pour former n moles d'eau en plus de la quantité d'eau produite si cet hydroxyde de sodium est carbonaté.

40 5. Procédé suivant la revendication 4, dans lequel un acide dicarboxylique et/ou un sel de mono-amine ou un sel de mono-ammonium de cet acide est ajouté dans l'étape (b), et dans lequel l'élimination azéotropique d'eau dans l'étape (a) est conduite de manière que soit vérifiée la relation :

$$A + C + 2D_2 \leq B$$

45 dans laquelle D_2 représente le nombre de moles d'acide dicarboxylique, de sel de mono-amine ou de sel de monoammonium d'acide dicarboxylique.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le solvant est le toluène ou le xylène.

7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'alkoxyalcanol contient 2 à 10 atomes de carbone par molécule.

50 8. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'acide sulfonique a un poids moléculaire compris entre 400 et 800.

9. Procédé suivant la revendication 2, dans lequel l'acide ou l'anhydride d'acide ajouté dans l'étape (b) est un acide ou anhydride d'acide polyisobuténylsuccinique.

10. Composition lubrifiante, comprenant une huile lubrifiante et 0,01 à 10 % en poids du sulfonate de sodium préparé par le procédé suivant l'une quelconque des revendications 1 à 9.

55 11. Composition lubrifiante suivant la revendication 10, qui contient également un dispersant sans cendres, un dialkyldithiophosphate de zinc et 5 à 500 ppm en poids de cuivre sous une forme soluble dans l'huile.

12. Composition de carburant, comprenant un carburant et un sulfonate de sodium fortement basique pré-

parés par le procédé suivant l'une quelconque des revendications 1 à 9.

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