

The present invention relates to a process for the production of N,N-disubstituted β -aminopropionic acids and their use as emulsifying agents, wetting agents, surfactants in cleaning agents and for the waterproofing of leather and furs, and in particular to a process for the production of N-alkyl-N(2-carboxyethyl)amides, novel N-alkyl-N(2-carboxyethyl)sulfonamides and N-alkyl-N(2-carboxyethyl)ureas, and to the use of these.

Alkylaminopropionic acids, alkyliminodipropionic acids, and the acylated alkylaminopropionic acids are known per se. Thus, US-PS 2.468.012 describes the production of N-alkylaminopropionic acids and their use as detergents, emulsifiers, and foam stabilizers. The production takes place by the addition of primary amines to acrylic acid esters and saponification of the resulting N-alkylaminopropionic acid esters to the corresponding acids or salts.

DE-OS 20 54 649 describes N-acyl-N-alkylaminopropionic acids that are produced by reaction of amines with acrylic acid derivatives, such as acrylic acid esters, acrylonitrile or acrylamide and subsequent reaction with anhydrides. In the last step of this synthesis the ester-, nitrile-, or amide function is saponified to acid. The products are obtained as an aqueous or aqueous-alcoholic solution.

These known production processes entail a number of disadvantages:

The saponification stage, which is absolutely essential, results in the fact that the products can only be obtained in solution, and not as a 100% substance without additional process steps. Only 20 to 30% solutions of a paste-like consistency can be obtained in water owing to the formation of gel structures. Only the concurrent use of alcohols, which is disadvantageous, makes it possible to raise the

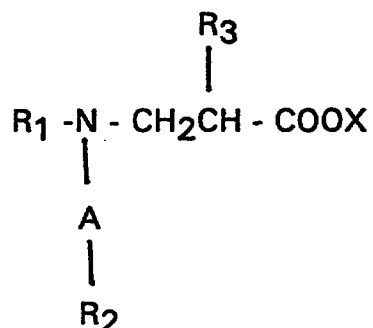
concentration to approximately 50%. Since the saponification is carried out in a strongly alkaline range, the products have a very high salt content, which is frequently undesirable, once the pH has been adjusted to 5 to 8, as is required for many applications, such as in the textile field.

When solid alkyl amines are used, the addition to the acrylic acid derivative must be carried out at elevated temperatures (above the melting point of the alkyl amine), because of which, with the reactive acrylic derivatives, the undesirable secondary reaction of diadduct formation is enhanced. During this secondary reaction a second molecule of acrylic derivative is added to the already formed N-alkyl-aminopropionic acid derivative, and this results in a tertiary amine, that cannot be acylated during the following synthesis step.

Finally, the odour of the residual content of acrylic ester or acrylonitrile in the product is also a disadvantage. A residual content of 0.1% acrylic ester can clearly be perceived.

It is the object of the present invention to provide a process that does not have the disadvantages set out above, in particular allows the production of the process products in substance without undesirably high additional salt contents and without the formation of undesirable by-products.

This object is achieved by a process for the production of compounds of the general formula I



wherein R_1 is a saturated or unsaturated alkyl radical or alkoxy-alkyl radical with 1-22 carbon atoms, preferably 12-18 carbon atoms,

R_2 is an alkyl radical with 1-18 carbon atoms, the oleoyl radical, a saturated or unsaturated carboxyalkyl radical with 3-4 carbon atoms, a carboxyphenyl radical, a carboxyl radical, or a toluyl radical,

R_3 is hydrogen or CH_3 , and

X is hydrogen, alkali metal, alkaline-earth metal, ammonium, alkylammonium or alkanolammonium, and

A stands for >C=O , >SO_2 , -CONH- , or an alkylene radical with 0-3 C-atoms,

with the proviso that

1) if A stands for an alkylene radical with 0-3 C-atoms, R_2 cannot mean an alkyl radical with 1-18 C-atoms or the oleoyl radical,

2) if A stands for >SO_2 or -CONH- , R_2 cannot be a saturated or unsaturated carboxyalkyl radical with 3-4 C-atoms, or a carboxyphenyl radical, or the carboxyl radical,

3) if A stands for >C=O , R_2 cannot be the carboxyl radical,

which process is characterized in that alkyl amines of the formula $\text{R}_1\text{-NH}_2$, wherein R_1 has the above meaning, are added to (meth)acrylic acid, and that the resultant N-alkylaminopropionic acids are reacted with carboxylic acid anhydrides, carboxylic acid chlorides, sulfonic acid chlorides, isocyanates, halogenated carboxylic acids, or (meth)acrylic acids and are then optionally neutralized, at least in part.

Surprisingly, it has been shown that alkylamines at 40 to 130°C, preferably 70 to 100°C, can be added to (meth)acrylic acid. Even though the components of the reaction are present as organic salt after mixing, the addition reaction is terminated after 1 - 4 hours and has achieved a complete conversion. No formation of diadduct is observed under these reaction conditions. No solvent is required. With amines having a boiling point below the so-called reaction temperatures, it is preferred that the reaction takes place under pressure, e.g., in an autoclave.

It is preferred that the reaction of alkylamine with (meth)acrylic acid takes place in equimolar quantities.

The following primary amines may be used as alkyl amines of the formula $\text{R}_1\text{-NH}_2$: methylamine, propylamine, butylamine, hexylamine, nonylamine, decylamine, dodecylamine, tridecylamine, isotridecylamine, hexadecylamine, octadecylamine, propoxypropyl amine,

octyloxypropyl amine, oleylamine, oleyloxypropyl amine, laurylamine, coconut oil amine, stearylamine, tallow fatty amine, or mixtures of the above amines. Laurylamine, coconut oil amine, tallow fatty amine and oleylamine are preferred amines.

The further reaction of the N-alkyl-N(2-carboxyethyl)-amine is carried out in substance with anhydrides, isocyanates, carboxylic acid chlorides, or sulfonic acid chlorides if it is an acylation. The acylating agent is used in equimolar quantities up to a slight excess (approximately 5%) at temperatures of 50 - 100°C.

The reaction with anhydrides or isocyanates is terminated after 1 - 2 hours and provides the desired N-alkyl-N(2-carboxyethyl) amides in 100-% form. When using monocarboxylic acid anhydrides, e.g., acetic anhydride, the monocarboxylic acid that occurs in equivalent quantities is separated off by distillation or by washing with water.

For example the following anhydrides can be used: acetic anhydride, propionic acid anhydride, butyric acid anhydride, maleic anhydride, succinic acid anhydride, phthalic acid anhydride.

As an example, the following isocyanates are suitable: butyl isocyanate, toluyl isocyanate, isopropyl isocyanate.

It is preferred that the second stage, i.e., the acylation reaction, is carried out with equimolar quantities of the reaction participants.

If the acylation reaction is carried out with carboxylic acid chlorides or sulfonic acid chlorides, powdered soda or tertiary amines are used as the acid-binding agents. The salt that is formed during the reaction can be filtered out or washed out with water.

The following are examples of carboxylic acid chlorides: acetic acid chloride, propionic acid chloride, oleic acid chloride, and suitable sulfonic acid chlorides, e.g., methane sulfonic acid chloride, ethane sulfonic acid chloride, and p-toluene sulfonic acid chloride.

The further reaction of the resulting N-alkylaminopropionic acid may also be effected with halogenated carboxylic acids, preferably chlorocarboxylic acids (e.g., chloroformic acid, chloroacetic acid, chloropropionic acid, chlorobutyric acid), or (meth)acrylic acid.

Using the new process, it is possible to produce the N,N-disubstituted β -aminopropionic acid derivatives according to the present invention in a single-vessel process in two synthesis stages without the formation of by-products. The products are obtained in 100-% form without solvents.

For neutralization, the N,N-disubstituted β -aminopropionic acid derivatives are mixed with aqueous solutions of alkali metal hydroxide, alkaline-earth metal hydroxide, or ammonia. Viscous or pasty aqueous solutions are obtained, depending on the concentration and the neutralizing agent.

In a preferred embodiment, neutralization is carried out with organic bases. Suitable organic bases in particular include primary, secondary, and tertiary amines. Examples of these are the alkylamines and alkanolamines. Especially preferred are the ethanolamines and isopropanol amines. The neutralizing agent may be added in quantities equivalent to the quantity of acid, or in smaller quantities than this.

The N,N-disubstituted β -aminopropionic acid derivatives and their salts are used as emulsifiers and wetting agents, or as surfactants in cleansing agents, which are not irritating the skin. A further field of

application is in formulations for waterproofing leather. Thus, the present invention also relates to a process for waterproofing leather and furskins by using the compounds according to the present invention, either alone or mixed with other known waterproofing agents.

The production of waterproof leather is substantially carried out according to the following two processes:

1. Filling the capillary-like, water-absorbing fibre spaces with waterproofing substances.

Substances that are insoluble in water, such as fats, paraffins, wax, or specific polymers also display the undesirable accompanying characteristic in that they affect the air and water vapour permeability which is important with regard to wearing comfort. Compounds that swell when they absorb water and thereby augment the natural swelling and sealing effect of the leather fibres behave in a more favourable manner. The products that are used in this method belong to the water-in-oil (W/O) class of emulsifiers.

2. Encasing the fibre bundles with waterproofing substances.

Emulsifiers that can form complexes with multivalent metal ions (cations) can in many cases also enter the chromium-collagen complex and then cause the water-repellency. Emulsifiers of this type are chemically bonded to the chromium- or aluminium-tanned leather fibres, and reduce the wettability and water absorption capacity by this hydrophobic encasement. The reduction of the ability to spread is seen in the formation of spherical droplets (the beading effect).

The requirements with respect to waterproof leather, which have risen dramatically during recent years, can scarcely be satisfied using known waterproofing methods, or can be met only by downgrading other important properties. Upper or shaft leather that is intended for daily use is today required to satisfy requirements that just a few years ago were imposed only on leather used for uniforms (military leather), without sacrificing any wearing comfort, fashionable appearance, and the like.

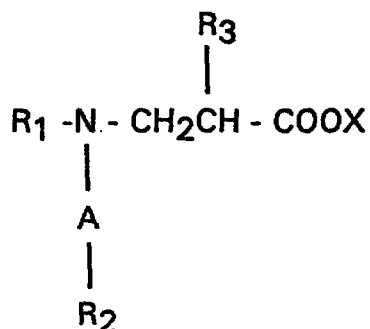
For this reason, processors have resorted, for example, to a two-step waterproofing process.

Leathers that have been finish-dried or dressed can be treated with silicones dissolved in organic solvents. A disadvantage in this respect is the drying temperature of between 90°C and 100°C that is required, for this leads to considerable losses of size. In addition, the high proportion of organic solvents that is released into the environment also causes a problem.

Particularly undesirable in the sense of rational finishing is the fact that a subsequent treatment involves an additional and unwanted stage in the processing cycle.

For this reason, it was an object of the present invention to provide a process for waterproofing leathers and furs, which is completed in a single stage, can be carried out in an aqueous liquor and in a vat, and with which it is possible to achieve simultaneous fat-liquoring and massive waterproofing.

This object is achieved by a process for waterproofing leather and furs characterized in that compounds of the general formula I



wherein R_1 is a saturated or unsaturated alkyl radical or alkoxy-alkyl radical with 1-22 carbon atoms, preferably 12-18 carbon atoms,

R_2 is an alkyl radical with 1-18 carbon atoms, the oleoyl radical, a saturated or unsaturated carboxyalkyl radical with 3-4 carbon atoms, a carboxyphenyl radical, a carboxyl radical ($-\text{COOH}$), or a toluyl radical,

R_3 is hydrogen or CH_3 , and

X is hydrogen, alkali metal, alkaline-earth metal, ammonium, alkylammonium or alkanolammonium, and

A stands for $>\text{C}=\text{O}$, $>\text{SO}_2$, $-\text{CONH}-$, or an alkylene radical with 0-3 C-atoms,

with the proviso that

1) if A stands for an alkylene radical with 0-3 C-atoms, R_2 cannot mean an alkyl radical with 1-18 C-atoms or the oleoyl radical,

2) if A stands for >SO_2 or -CONH- , R_2 cannot be a saturated or unsaturated carboxyalkyl radical with 3-4 C-atoms, or a carboxyphenyl radical, or the carboxyl radical,

3) if A stands for >C=O , R_2 cannot be a carboxyl radical,

are allowed to react with the leather or furs to be treated, either during or after retanning, in an amount of 0.1 - 25% by weight, preferably 1 to 15% by weight, relative to the shaved weight of the leather or the wet weight of the furs, at a pH of 4 to 9, that the pH is subsequently set to the range from 3.5 to 5.0, and that after the treatment fixation is optionally effected with a 2-, 3- or 4-valent metallic salt, preferably in aqueous solution.

The products according to the present invention are used for water-proofing either directly in their at least partially neutralized form, as a product that contains some water, mostly of a paste-like consistency, or the non-neutralized, mostly paste-like products are dissolved in hydrocarbons and/or chlorinated hydrocarbons, optionally by means of solubilizers, and then at least partially neutralized. The bases mentioned above, particularly organic primary, secondary, and tertiary amines and alkanolamines, as well as aqueous solutions of ammonia and alkali hydroxides, are suitable for this. The emulsifying effect of the neutralized products also allows the formulation of water-containing products.

The products according to the present invention are used in a quantity of 0.1 to 25, preferably 1 to 15%-wt., relative to the shaved weight of the leather or to the wet weight of the furs, at pH-values between 4 and 9; subsequently, the pH-value is reduced to 3.5 to

5.0. An optional fixation can be effected by means of a 2-, 3-, or 4-valent metal salt.

The product according to the present invention used for waterproofing advantageously comprises 5 to 80%-wt., preferably 10 - 70%-wt. of the compounds according to the present invention, of the general formula I, optionally 20 to 70%-wt., preferably 30 - 60%-wt. of hydrocarbons and/or chlorinated hydrocarbons, optionally with solubilizers, such as the higher-boiling point products of the oxosynthesis. The remainder to 100% is water.

Even though excellent fat-liquoring and waterproofing can be achieved with the compounds according to the present invention alone, the waterproofing agents according to the present invention may be used together with known fat-liquoring and greasing and/or waterproofing agents, such as phosphoric acid partial esters, silicone oils, oleic acid sarcoside and/or (chloro)paraffins.

Insofar as phosphoric acid partial esters are used, it is preferred that partial esters of alcohols with a chain length of C₄ to C₂₀, preferably C₁₆-C₁₈ be used, these being optionally oxalkylated, in quantities from 0.5 to 30%-wt., preferably 1 - 20%-wt. (relative to 100 g waterproofing agent).

The co-application of acidic phosphoric acid esters can be such that they are prepared together with the compounds according to the present invention, diluted, and then neutralized together with these. The phosphoric acid esters can also be used in already neutralized form. The phosphoric acid esters are used, for example, to reduce

the extractable content of fat; this is a particular advantage for garment leathers because of the improved resistance to dry-cleaning that it brings about.

If silicone oils are used in addition to the compounds according to the present invention, they are used in quantities of from 0.5 to 80%-wt., preferably 1 - 20%-wt. (relative to 100 g of the waterproofing-agent formulation).

Commercially available polysiloxanes, such as dimethyl- or methyl-phenylpolysiloxane may be used as silicone oils. Viscosity ranges from 100 to 500 mPa.s are preferred. The silicone oil is prepared together with the compound according to the present invention, optionally together with hydrocarbons and/or chlorinated hydrocarbons, or solubilizers. The use of silicones preferably assists in achieving specific desirable surface effects such as smoothness of grain.

It is also possible to use oleic acid sarcoside in order to obtain improved softness and a more comfortable feel. In general, any combination of phosphoric acid partial ester, silicone oil, and oleic acid sarcoside can be used with the compounds according to the present invention in order to achieve specific effects.

Oleic acid sarcoside may also be used in addition to the compounds according to the present invention, in quantities of 0.5 to 50%-wt., preferably 2 - 20%-wt. (relative to 100 g of the formulation used).

The invention will be described in more detail by the examples that follow.

Example 1:

534 g (2 mol) oleylamine is prepared in a flask having a stirrer, a thermometer, and a condenser, and heated to 60°C. Within 30 minutes, 144 g (2 mol) acrylic acid is added by drops, whereupon the temperature rises to approximately 90°C. Stirring is then continued for a further 2.5 hours at 90°C. Complete conversion is ascertained by determining the primary bases. The reaction product is cooled to 70°C and 196 g (2 mol) maleic anhydride is added by portions. In order to complete the reaction, stirring is continued for 2 hours at 70 - 80°C. The N-oleyl-N(2carboxyethyl) maleic acid monoamide is obtained as a light brown paste.

Acid value 250 mg KOH/g

Residual content of basic nitrogen: 0.2 mmol/g

122 g (2 mol) monoethanolamine is added dropwise at 80°C under stirring for neutralization.

Example 2:

As in Example 1, 269 g (1 mol) stearylamine is added to 72 g (1.0 mol) acrylic acid, and the reaction product is reacted with 98 g (1 mol) maleic anhydride. The N-stearyl-N(2-carboxyethyl) maleic acid monoamide solidifies at room temperature to form a light-brown paste.

Acid value: 251 mg KOH/g

Residual content of basic nitrogen: 0.32 mmol/g

Neutralization is effected at 100°C with 37.5 g (0.5 mol) isopropanol amine.

Example 3:

As in Example 1, 486 g (2.0 mol) lauryloxypropyl amine is added to 144 g acrylic acid (2.0 mol) and the reaction product is reacted with 196 g (2 mol) maleic anhydride. The N-lauryloxypropyl-N(2-carboxyethyl) maleic acid monoamide solidifies at room temperature to form a dark-brown, slightly cloudy paste.

Acid value: 265 mg KOH/g
Residual content of basic nitrogen: 0.3 mmol/g

Example 4:

As in Example 1, 785 g coconut oil amine (3.72 mol; content of basic nitrogen: 4.74 mmol/g) is added to 268 g acrylic acid (3.72 mol), and the reaction product is reacted with 364.8 g (3.72 mol) maleic anhydride. A reddy-brown, highly viscous oil is obtained.

Acid value: 290 mg KOH/g
Residual content of basic nitrogen: 0.25 mmol/g

554 g (3.72 mol) triethanolamine is added by drops at 80°C during stirring for neutralization.

Example 5:

As in Example 1, 101 g (1.0 mol) hexylamine is added to 72 g (1.0 mol) acrylic acid, and the reaction product is reacted with 98 g (1.0

mol) maleic anhydride. The N-hexyl-N(2-carboxyethyl) maleic acid monoamide is obtained as a light-brown oil.

Acid value: 418 mg KOH/g

Residual content of basic nitrogen: 0.15 mmol/g

Example 6:

534 g (2 mol) oleylamine is heated to 60°C in a flask equipped with a stirrer, a thermometer, and a condenser. Within 30 minutes, 172 g (2 mol) methacrylic acid is added by drops, whereupon the temperature rises to approximately 85°C. In order to complete the reaction, the mixture is stirred for 3 h at 100°C. A complete reaction is ascertained by determining the primary bases. Cooling to 70°C is then effected, and 204 g (2 mol) acetic anhydride is added in drops at 70 - 80°C. After a further 2 hours, the resulting acetic acid is distilled off at a vacuum of 20 mbar. The N-oleyl-N(2-carboxy-2-methylethyl) acetamide is obtained as a brown, clear oil.

Acid value: 139 mg KOH/g

Residual content of basic nitrogen: 0.1 mmol/g

This is neutralized at 80°C with 112.2 g (2 mol) KOH, dissolved in 2492 g water. An aqueous solution with 25% solids is obtained.

Example 7:

As in Example 1, 267 g (1.0 mol) oleylamine is added to 72 g (1.0 mol) acrylic acid. Next, 148 g (1.0 mol) phthalic acid anhydride is added in portions at 90°C and stirred for 3 hours at 100°C. The N-

oleyl-N-(2-carboxyethyl) phthalic acid monoamide is a yellowish-brown paste.

Acid value: 225 mg KOH/g

Residual content of basic nitrogen: 0.5 mmol/g

Example 8:

As in Example 1, 267 g oleylamine is added to 72 g acrylic acid. The addition product is mixed with 55 g of anhydrous sodium carbonate, and 301 g (1.0 mol) oleic acid chloride is added by drops at 100°C within approximately 2 hours. After a further 2 hours the acylation is ended. The common salt that is formed is washed out with water.

Acid value: 94 mg KOH/g

Residual content of basic nitrogen: 0.1 mmol/g

Example 9:

As in Example 6, 267 g (1.0 mol) oleylamine is added to 86 g (1.0 mol) methacrylic acid.

After the addition, 101 g (1.0 mol) triethylamine is added to the reaction mixture and 190.5 g (1.0 mol) p-toluenesulfonic acid chloride is added by portions at 70 - 90°C. After termination of the exothermic reaction, stirring is carried out for 2 hours at 90°C, and then the salt is washed out with water. The N-oleyl-N(2-carboxy-2-methyl-ethyl) p-toluenesulfonic acid amide is obtained as a dark-brown, viscous oil.

Acid value: 99 mg KOH/g

Residual content of basic nitrogen: 0 mmol/g

IR: C = O 1720 cm^{-1}
 C = C 1620 cm^{-1} (aromatic compound)
 SO₂ - N 1330 cm^{-1} and 1170 cm^{-1}

H-NMR: δ 7 - 8 ppm aromatic protons

105 g (1.0 mol) diethanolamine is added whilst stirring at 90°C for neutralization.

Example 10:

As in Example 1, 267 g (1.0 mol) oleylamine is added to 72 g (1.0 mol) acrylic acid.

After the addition, 53 g (0.5 mol) powdery sodium carbonate is added and 114.5 g (1.0 mol) methane sulfonic acid chloride is added by drops at 110°C . Stirring is continued for a further 2 hours at 110°C for post reaction. The resulting salt is washed out with water. The N-oleyl-N(2-carboxyethyl)methane sulfonic acid amide is obtained as dark-brown paste.

Acid value: 129 mg KOH/g
 Residual content of basic nitrogen: 0 mmol/g

IR: C = O 1730 cm^{-1}
 SO₂-N 1320 cm^{-1} and 1160 cm^{-1}

Example 11:

As in Example 1, 267 g (1.0 mol) oleylamine is added to 72 g (1.0 mol) acrylic acid.

After the addition, 115 g (1.0 mol) N-ethylmorpholine is added, and 133 g (1.0 mol) toluylisocyanate is added by drops at 40 - 50°C. This is allowed to react for 1 hour; N-oleyI-N(2-carboxyethyl)-N'-toluyl urea is obtained as a brown oil.

Acid value:

89 mg KOH/g

IR: C = O (acid) 1720 cm^{-1}
 N-C=O 1660 cm^{-1} and 1560 cm^{-1}
 C = C (aromatic) 1590 cm^{-1} and 1610 cm^{-1}

Example 12:

As in Example 1, 267 g (1.0 mol) oleylamine is added to 72 g (1.0 mol) acrylic acid.

After the addition, 115 g (1.0 mol) N-ethylmorpholine is added, and 99 g (1.0 mol) n-butyIisocyanate is added by drops at 40 - 50°C. This is allowed to react for 1 hour. N-oleyI-N(2-carboxyethyl)-N'-butyl urea is obtained as a light-brown oil.

Acid value:

96.4 mg KOH/g

IR: C = O (acid) 1720 cm^{-1}
 N-C=O 1620 cm^{-1} and 1540 cm^{-1}

Example 13:

As in Example 1, 204 g oleylaminopropionic acid (0.6 mol), 70 g chloroacetic acid (sodium salt; 0.6 mol), 54 g water, and 108 g isopropanol are prepared and heated to 80°C; this results in a clear solution. 106.6 g 45% sodium hydroxide solution (1.2 mol) is added to

this solution by drops within 45 minutes, whereupon the viscosity of the reaction mixture increases. This is stirred for 4 hours at 82°C, then neutralized with concentrated hydrochloric acid and poured into an excess amount of water, whereupon the product precipitates. The product (N-oleyl-N-carboxymethyl-aminopropionic acid) is separated and dried.

Acid value: 245 mg KOH/g

The addition product used as the starting product is obtained, as in Example 1, from the reaction of oleylamine with acrylic acid in equimolar quantities.

Example 14:

267.5 g oleyl amine (1.0 mol) and 0.2 g HQME (hydroquinone monomethyl ether) are prepared. 144 g acrylic acid (2.0 mol) is added to this by drops during cooling to a temperature of at most 70°C, and this is followed by heating to 140°C. From 80°C, the reaction proceeds exothermically and the viscosity increases sharply. After approximately 10 minutes at 120°C the mixture becomes paste-like. It is then stirred for another 3 hours at 140°C. The product (N-oleyl-N(2-carboxyethylaminopropionic acid) has an acid value of 253 mg KOH/g.

Example 15:

a) 13.6 g water and 22.7 g 45% sodium hydroxide solution are prepared and heated to approximately 50°C in a stirring vessel. Next, and while stirring, 63.7 g N-oleyl-N-(2-carboxyethyl) maleic acid monoamide of Example 1 is added, and subsequently stirred until homogeneous.

b) The product from a) was used in the following composition for the production of waterproof leather, and the water repellent action was examined:

Cattle hides:

Type: waterproof

Material:

Cattle hides, wet blue

Shaved substance: 2.0 mm

Percentages relative to shaved weight

Washing:

300% water 35°C

+ 0.5% acetic acid 1:5* 15 min.

*1 part/vol. conc. acetic acid and 5
part/vol. water

Drain off bath

Washing:

300% water 35°C 10 min.

Drain off bath

Neutralization/

150% water 35°C

Dyeing/

2% Na-formiate undissolved 90 min.

Retanning

+ 2% dye undissolved 15 min.

+ 4% Tanigan QF** undissolved 30 min.

+ 12% Kastanie N undissolved 60 min.

at 8 rpm overnight

+ 250% water 60°C 10 min.

Drain off bath

Washing: 300% water 60°C 10 min.
Drain off bath

Waterproofing: 100% water 60°C
+ 0.5% ammonia 1:5* 2 min.
*1 part/vol. conc. ammonia and
5 part/vol. water
+ 6.3% of the waterproofing agent
according to the present
invention of Example 15a
1:5 * 60 min.
*1 part/vol. product and 5 parts/vol.
water
+ 0.5% formic acid 1:5 15 min.
pH: 3.6 - 4.0

Drain off bath

2 x Washing: 300% water 40°C each 10 min.
Drain off bath

Fixation: 150% water 40°C
3% Baychrom A** undiss. 60 min.
pH: 4.2 - 4.8

Drain off bath

3 x Washing: 300% water 20°C each 10 min.
Drain off bath

Horse up overnight, samming, setting out, vacuum drying (80 °C/2 min.), air-off, acclimatizing, staking, ironing (80°C/0.5 min.)

****)** products of BAYER AG, Leverkusen

Bally penetrometer: (10% amplitude)

Water penetration time: >7/>7 hours

Water absorption in %:

after 7h: 9.9/10.4

Maesertest:

Flexes: 21924/19207

Water absorption in %:

after flexes: 8.0/7.1

Example 16:

The amide produced in Example 1 is used. 30 g water and 7 g diisopropanol amine are placed in a stirring flask at 50°C before the organic phase, consisting of 14 g of the amide according to the present invention, 3.5 g phosphoric acid ester amine salt (produced by reaction of Alfol 16-18, a mixture of fatty alcohols from the Ziegler synthesis, with P₂O₅, molecular ratio 3:1, diisopropanol amine for neutralization), and 45.5 g chloroparaffin containing 40% chlorine in the chain, is introduced during stirring, and mixed homogeneously.

This formulation is used in the following recipe to produce military leather:

Cattle hides:

Type: military leather

Material: Cattle hides, wet blue
shaved substance: 2.0 mm

Percentage relative to shaved weight

Washing: 300% water 35°C
0.5% formic acid 1:5* 15 min.
* 1 part/vol. conc. acid with 5 part/vol.
Water

Drain off bath

Neutralization: 100% water 35°C
3% Na-formiate undissolved 15 min.
pH: 4.4
+ 0.5% Na-bicarbonate 1:10 90 min.
pH: 4.8

Drain off bath

Washing: 300% water 30°C 10 min.
Drain off bath

Retanning: 200% water 30°C
1% dye 1:20 20 min.
+ 4% Tanigan**QF undissolved 30 min.
+ 12% Quebracho undissolved 60 min.
Automatic run overnight
Rest/run 15 min./1 min.
+ 200% water 60 °C 20 min.

Drain off bath

Washing: 300% water 60°C 10 min.
Drain off bath

Waterproofing: 200% water 60°C
10% of the waterproofing agent
according to Example 16
diluted with water in proportion of 1:5 (vol/vol) 60 min.
+ 1% formic acid 1:5* 15 min.
+ 1 part/vol. conc. acid and 5 parts/vol.
water
+ 3% Baychrom**F undissolved 60 min.
pH: 3.6 - 3.7

Drain off bath

3 x Washing: 300% water 25°C each 10 min.
Drain off bath

Rinsing: W a t e r 20°C 10 min.

Horse up overnight, samming, setting-out, vacuum drying (80°C/3 min.), air-off, staking, ironing (80°C/0.5 min.)

** products of BAYER AG, Leverkusen

Bally penetrometer: (10% amplitude)
Water penetration time: >420/>420 min.
Water absorption in %:
after 7 h: 12/14

Maesertest

Flexes: 29785/25971

Water absorption in %

after flexes: 10/12

Example 17:

a) 30.5 g water and 5.5 g 45% sodium hydroxide solution are prepared in a stirring vessel at approximately 50°C. The organic phase, consisting of 18 g of the amide of Example 1, 40 g of a higher boiling mineral oil, and 6 g dimethylpolysiloxane having a viscosity of 350 mPa.s, is slowly added while stirring, and then stirred until homogeneous.

b) The formulation of a) was used in a formulation as in Example 16, and provided the following results:

Bally penetrometer: (10% amplitude)

Water penetration time: >420/>420 min.

Water absorption in %

after 7h: 7/8

Maesertest:

Flexes: >48123/>48316

Water absorption in %

after flexes: 9/8

Example 18:

The amide according to the present invention of Example 1 is used.

39 g water with 3 g 45% sodium hydroxide solution are placed in a stirring vessel at approximately 50°C. Then the organic phase, consisting of 6 g of the amide of Example 1, 6 g oleic acid sarcoside, 40 g of a higher-boiling mineral oil, and 5 g dimethylpolysiloxane having a viscosity of 350 mPa.s, is slowly introduced during stirring and then homogenized.

The product so obtained was used in the formulation for waterproofing according to Example 16b); the following results were obtained:

<u>Bally penetrometer:</u>	(10% amplitude)
<u>Water penetration time:</u>	>420/>420
<u>Water absorption in %</u>	
after 7 h:	9/10
<u>Maesertest:</u>	
Flexes:	29885/30147
<u>Water absorption in %:</u>	
after flexes:	14/11.6

Example 19:

a) 39 g water and 4 g 45% sodium hydroxide solution are placed in a stirring vessel at approximately 50°C. Whilst stirring, the organic phase, consisting of 12 g of the amide according to Example 4, 35 g higher-boiling hydrocarbon, 5 g dimethylpolysiloxane having a viscosity of 100 mPa.s, and 5 g phosphoric acid partial ester (Alfol 12-18, reacted with P₂O₅, molar ratio 3:1), is introduced and stirred until homogeneous.

b) Used in the formulation according to Example 16, the following results were obtained:

<u>Bally penetrometer:</u>	(10% amplitude)
<u>Water penetration time:</u>	> 7 / > 7 hours
<u>Water absorption in %</u> after 7 h:	13.3/12.0

Maesertest

Flexes:	15849/16717
<u>Water absorption in %</u> after flexes:	12/8

Example 20:

The product described in Example 13 was used. To this end, 20 g of this substance was placed with 68.4 g of a chloroparaffin with 40% chain-chlorine in a stirring vessel and stirred at 100 to 105°C until homogeneous. After cooling to approximately 70°C, 11.6 g diisopropanol amine was added to the mixture for neutralization.

This formulation was used in the following composition to produce waterproof leather, and examined with regard to its effect:

<u>Material:</u>	Cattle hides, wet blue
	Shaved substance: app. 2.0 mm

Percentages relative to shaved weight

<u>Washing:</u>	300% water	35°C	
	0.5% acetic acid	1:5	15 min.
Drain off bath			

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<u>Waterproofing:</u>	100% water	60°C	
<u>Fixation:</u>	8% waterproofing agent	1:4	60 min.
	+	1% formic acid	1:5
	+	3% Baychrom F	60 min.
		pH of bath: 3.6 - 3.7	

Drain off bath

3 x Washing: 300% water 25°C each 10 min.

Drain off bath

Horse up overnight, samming, setting out, vacuum drying, (80-85°C/2 min.), air-off, moisten, staking, vacuum ironing (80-85°C/30 sec.). No unusual observations were made during the wet processing stage.

Bally penetrometer: (10% amplitude)

Water penetration time: : >7/>7 hours

Water absorption in %:

after 7 h 13.1/8.2

Maesertest:

Flexes 15407/14320

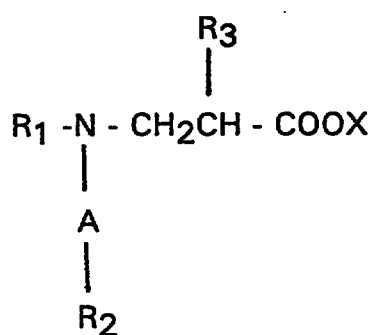
Water absorption in %

after flexes 7.7/5.0



CLAIMS

1. A process for the production of compounds of the general formula I



wherein R_1 is a saturated or unsaturated alkyl radical or alkoxy-alkyl radical with 1-22 carbon atoms, preferably 12-18 carbon atoms,

R_2 is an alkyl radical with 1-18 carbon atoms, the oleoyl radical, a saturated or unsaturated carboxyalkyl radical with 3-4 carbon atoms, a carboxyphenyl radical, a carboxyl radical, or a toluyl radical,

R_3 is hydrogen or CH_3 , and

X is hydrogen, alkali metal, alkaline-earth metal, ammonium, alkylammonium or alkanolammonium, and

A stands for >C=O , >SO_2 , -CONH- , or an alkylene radical with 0-3 C-atoms,

with the proviso that



1) if A stands for an alkylene radical with 0-3 C-atoms, R₂ cannot mean an alkyl radical with 1-18 C-atoms or the oleoyl radical,

2) if A stands for >SO_2 or -CONH- , R₂ cannot be a saturated or unsaturated carboxyalkyl radical with 3-4 C-atoms, or a carboxyphenyl radical, or a carboxyl radical,

3) if A stands for >C=O , R₂ cannot be a carboxyl radical,

which process is characterized in that alkyl amines of the formula R₁-NH₂, wherein R₁ has the above meaning, are added to (meth)-acrylic acid at temperatures of 40 - 130°C, and that the resultant N-alkylaminopropionic acids are reacted with carboxylic acid anhydrides, carboxylic acid chlorides, sulfonic acid chlorides, isocyanates, halogenated carboxylic acids, or (meth)-acrylic acids and are then optionally neutralized, at least in part.

2. The process according to claim 1 characterized in that the addition of alkylamines to (meth)acrylic acid is carried out at temperatures of 70° - 100°C.

3. The process according to claims 1 and 2 characterized in that alkylamines and methacrylic acid are reacted in equimolar quantities.

4. The process according to any one of claims 1 to 3 characterized in that the reaction is carried out under pressure, if alkylamines which boil below the reaction temperatures are used.

5. The process according to any one of claims 1 to 4 characterized in that the N-alkylaminopropionic acids produced in the first step are



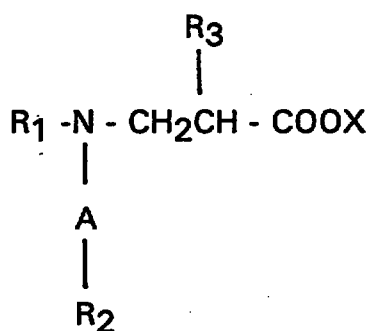
reacted with carboxylic acid anhydrides, carboxylic acid chlorides, sulfonic acid chlorides, isocyanates, haloacid, or (meth-)acrylic acids at temperatures of 50 to 100°C.

6. The process according to any one of claims 1 to 5 characterized in that carboxylic acid anhydride, carboxylic acid chloride, sulfonic acid chloride, isocyanate, halogenated carboxylic acid, or (meth-)acrylic acids are used in an equimolar ratio or in slight excess, preferably up to 5%, relative to the N-alkylaminopropionic acid.

7. The process according to any one of claims 1 to 6 characterized in that acid-binding agents, preferably powdery sodium carbonate or tertiary amines, are added, if carboxylic acid chlorides, sulfonic acid chlorides, or haloacids are used for the second stage of the reaction.

8. The process according to any one of claims 1 to 7 characterized in that the neutralization is carried out with organic bases, preferably alkylamines and alkanolamines, in particular ethanolamines or propanolamines.

9. N-alkyl-N(2-carboxyethyl)sulfonamides or ureas of the general formula I

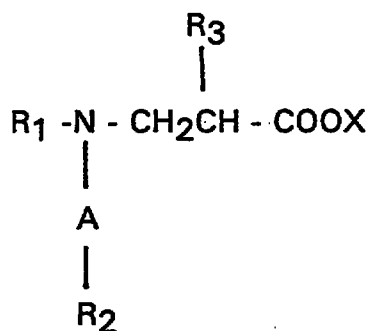




wherein R_1 , R_2 , R_3 , and X have the meaning as stated in claim 1, characterized in that A stands for $SO_2=$ or $-CONH-$, with the proviso that

R_2 cannot be an alkyl radical with 1 - 18 C-atoms, a saturated or unsaturated carboxyalkyl radical with 3 - 4 C-atoms, a carboxyphenyl radical, a carboxyl radical, or a toluyl radical.

10. A process for waterproofing leather and furs characterized in that compounds of the general formula I



wherein R_1 is a saturated or unsaturated alkyl radical or alkoxy-alkyl radical with 1-22 carbon atoms, preferably 12-18 carbon atoms,

R_2 is an alkyl radical with 1-18 carbon atoms, the oleoyl radical, a saturated or unsaturated carboxyalkyl radical with 3-4 carbon atoms, a carboxyphenyl radical, a carboxyl radical, or a toluyl radical,

R_3 is hydrogen or CH_3 , and



X is hydrogen, alkali metal, alkaline-earth metal, ammonium, alkylammonium or alkanolammonium, and

A stands for >C=O , >SO_2 , -CONH- , or an alkylene radical with 0-3 C-atoms,

with the proviso that

1) if A stands for an alkylene radical with 0-3 C-atoms, R_2 cannot mean an alkyl radical with 1-18 C-atoms or the oleoyl radical,

2) if A stands for >SO_2 or -CONH- , R_2 cannot be a saturated or unsaturated carboxyalkyl radical with 3-4 C-atoms, or a carboxyphenyl radical, or a carboxyl radical,

3) if A stands for >C=O , R_2 cannot be a carboxyl radical,

are allowed to react with the leather or furs to be treated, either during or after retanning, in an amount of 0.1 - 25% by weight, preferably 1 to 15% by weight, relative to the shaved weight of the leather or the wet weight of the furs, at a pH of 4 to 9, that the pH is subsequently set to the range from 3.5 to 5.0, and that after the treatment fixation is optionally effected with a bivalent, trivalent or tetravalent metallic salt, preferably in aqueous solution.

11. The process according to claim 10 characterized in that a product is used for the waterproofing that comprises 5-80, preferably 10-70%-wt. of compounds of the general formula I, preferably in at least partially neutralized form, optionally 20-70, preferably 30-60%-wt. of



hydrocarbons, optionally solubilizers, and water as remainder to 100%.

12. The process according to any one of claims 10 to 11 characterized in that the employed waterproofing agent comprises phosphoric acid partial esters of optionally oxalkylated alcohols of the chain length C_4 to C_{20} , preferably C_{16} - C_{18} , in amounts of 0.5 to 30, preferably 1 to 20%-wt., relative to 100 g of the waterproofing agent that is used.

13. The process according to any one of claims 10 to 12 characterized in that the waterproofing agent comprises silicone oils, preferably dimethyl or methylphenyl polysiloxanes, in amounts of 0.5 to 80, preferably 1 to 10%-wt., relative to 100 g of the waterproofing agent that is used.

14. The process according to any one of claims 10 to 13 characterized in that the waterproofing agent comprises 0.5 to 50, preferably 2 to 20%-wt. of oleic acid sarcoside, relative to 100 g of the waterproofing agent.

15. The process according to any one of claims 10 to 14 characterized in that the waterproofing agent comprises paraffins and/or chloroparaffins.