Patented Jan. 9, 1945

2,367,010

UNITED STATES PATENT OFFICE

2,367,010

AMIDES AND SULPHONATED DERIVATIVES THEREOF

Gifford D. Davis, South Orange, N. J., Donald Price, New York, N. Y., and John G. Milligan, Arlington, N. J., assignors to National Oil Products Company, Harrison, N. J., a corporation of New Jersey

No Drawing. Application August 14, 1941, Serial No. 406,842

19 Claims. (Cl. 260—401)

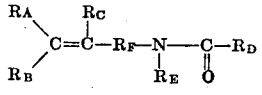
This invention relates to amides and their sulphonated derivatives, and more particularly to sulphonated amides having surface active properties.

There has been developed a class of surface active compounds which consist of fatty radicals coupled by esterification, amidification, or by other means to a short organic chain which is in turn coupled to a sulphate or sulphonate group. Such compounds have certain disadvantages, among which is the susceptibility to hydrolysis of the linkages between the short organic chain and the fatty residue and the sulphate group. Further, the materials from which such compounds are made are in many cases expensive and difficultly procurable.

Accordingly, it is an object of this invention to provide surface active materials which will be relatively stable to hydrolysis.

Another object is to provide surface active materials which can be made from readily and cheaply procurable raw materials.

The above and other objects are secured by this invention in a class of compounds having the general formula:



wherein:

R_A, R_B and R_C indicate hydrogen atoms or alkyl radicals containing less than 5 carbon atoms, which are so chosen that at least one of the double bonded carbons to which they are attached will be a tertiary carbon atom;

R_D indicates a fatty acid residue containing at least 7 carbon atoms;

R_E indicates hydrogen or an alkyl, aryl, alphyl or cyclo-aliphatic group;

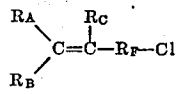
R_F indicates an organic linking group containing from 1 to 4 carbon atoms.

Amides according to the above formula are resistant to alkaline hydrolysis and are useful as such for various purposes, for example, as insecticides, solvents, textile lubricants and softeners, synthetic wax ingredients and the like. Moreover, these amides, upon sulphonation, yield products which have excellent detergent, emulsifying and wetting properties, and which are also exceptionally resistant to alkaline hydrolysis. Due to the fact that one of the double-bonded carbon atoms is tertiary, a true sulphonate is apparently formed.

As aforementioned, the selection of the radicals R_A, R_B and R_C must be made in such a manner as to provide an olefinic tertiary carbon atom. Hence if R_C is to be a hydrogen atom then both R_A and R_B will have to contain a carbon atom to render the double-bonded C on the left of the double bond a tertiary carbon atom. In the event that R_C contains a carbon atom, then the double-bonded carbon atom to which it is attached will be an olefinic teriary carbon atom and R_A and R_B may be either hydrogens or alkyl groups as desired.

By proper selection of the radicals R_D and R_E, different relative wetting, emulsifying and detergent effects may be obtained, equal size in the radicals R_D and R_E tending to increase wetting power.

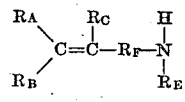
Compounds of the type contemplated by this invention may be prepared in any conventional manner, but are preferably made by reacting an appropriate organic chloride containing an olefinic tertiary carbon atom having the general formula, using the same letter notations given above:



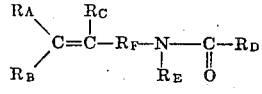
with ammonia or a primary amine;



to form an intermediate amine having the formula:



which is in turn reacted with an acylating agent containing the radical R_D to form the class of amides comprising this invention;



which may be finally sulphonated to produce a highly active and highly stable surface active agent.

Referring to the tertiary unsaturated chlorides used in the manufacture of the novel products of this invention, the preferred chlorides coming under the general formula appearing above are 2-methyl allyl chloride, commonly designated as methallyl chloride, and derivatives thereof, in which the chlorine atom is linked to a carbon atom which is in turn linked to a tertiary olefinic carbon atom, as the chlorine in such a configuration is very active and condenses very readily with the amine in the reaction set forth above. However, excellent products are obtainable wherein the tertiary carbon atom is not adjacent the carbon atom to which the chlorine atom is linked in the chloride compound. Compounds suitable for use in making the compounds of this invention include methallyl chloride, 2-ethylallyl chloride, 2-methyl crotonyl chloride, 3-methyl crotonyl chloride, and the like. In general, the substituents attached to the allyl residue should be relatively short, preferably containing less than 5 carbon atoms each. Chlorides of these types may readily and cheaply be obtained by the chlorination of certain unsaturated hydrocarbons, as by the methods described in "Industrial and Engineering Chemistry" vol. 31, page 1413, et seq. (1939). Chlorides of the unsaturated compounds have been given above as suitable materials; obviously, however, analogous compounds of other halogens may be employed.

With reference to the amino-compound used in producing the amides of this invention, this may be ammonia or an aliphatic, cycloaliphatic, aromatic or hydroaromatic primary amino compound, such as methyl, ethyl, propyl, isopropyl, butyl and like amines; cyclohexylamine; aniline and its homologues; or benzylamine and the like. The choice of amino compound employed will be determined by the properties desired in the final sulphonated product; in general, the amines with the larger organic groups tend to emphasize the wetting properties of the final sulphonated products.

The acylating agents used in making the products of this invention may be any higher fatty acids containing 8 to 30 carbon atoms, or derivatives thereof capable of condensing with the intermediate amine. It is preferred, however, to employ the acyl chlorides corresponding to the aforementioned acids. The acid residues of these acids should contain from 7 to 29 carbon atoms. preferably 11 to 13 carbon atoms. The fatty acid itself or glyceride or other ester thereof; or any mixture of fatty acids, acyl chlorides or esters derived from a fatty material; or any fatty glyceride-containing fat, may be employed as acylating agents under suitable conditions. Suitable acids and acid chlorides are capric, lauric, myristic, palmitic, stearic, oleic and the like; or acids and acid chlorides derived from the mixed acyl residues contained in coconut, palm and the like natural oils and fats. Examples of the fats which may be used directly as acylating agents are tallow, coconut oil, palm oil, olive oil and the like.

The condensation between the unsaturated chloride and the amino-compound is brought about by mixing these compounds and heating between about 20° C. and about 150° C., preferably 90° C. to 100° C., with agitation for about 1 to 5 hours. The unsaturated amines formed in this reaction may be separated from the reaction mixture by liberation from their salts (hydrochlorides), if necessary, followed by fractional distillation, extraction with solvents, or other suitable means depending on the physical and chemical properties of the amines.

The unsaturated intermediate amine may be amidified by the fatty acylating agent in any usual manner, but this is most advantageously done by running an acyl chloride slowly, with cooling, into a solution of the amine, with or without an acid neutralizing agent, in a suitable inert solvent. The amide can be extracted from the reaction mixture with ether. Suitable acid-neutralizing agents are pyridine, potassium hydroxide, sodium carbonate, sodium hydroxide, and their equivalents; suitable inert solvents are dioxane, ether, carbon tetrachloride, heptane, ethylene dichloride and the like.

The sulphonation of the amide may be brought about in any suitable way, as by treating the amide with acetic anhydride and concentrated sulphuric acid at room temperature for about ½ hour. The resultant material is chilled, diluted with water, neutralized and extracted with a suitable solvent such as butanol. Oleum and chlorsulphonic acid likewise may be employed as sulphonating agents.

With the foregoing discussion in mind, the following specific examples are given, which examples are to be taken as illustrative merely, and not in any limiting sense. All parts given are by weight.

EXAMPLE I

Sulphonated methallyl butyl lauramide

585 parts of butyl amine were refluxed on a steam bath with stirring. 181 parts of methallyl chloride were added slowly, and refluxing continued for one hour. Thereafter the mixture was distilled under a column until practically all the unreacted butyl amine was removed. The residue was treated with 200 parts of 50% aqueous sodium hydroxide, and the resulting upper layer containing the liberated methallyl butyl amine was separated and fractionally distilled. Methallyl butyl amine distilled between 152° and 155° C.

5 parts of a methallyl butyl amine prepared as above described were dissolved in 4 parts of pyridine and 10 parts of dioxane. 9 parts of lauric acid chloride were added slowly with external cooling. The mixture was extracted with 100 parts of ether. The ether extract solution was washed successively with 100-part portions of 5% aqueous hydrochloric acid, and then with 5% aqueous sodium hydroxide until all the lauric acid present was washed out; and finally with water until neutral. The ether was distilled from the solution to leave the methallyl lauramide as a colorless liquid.

141 parts of methallyl lauramide obtained as above described were mixed with 61 parts of acetic anhydride, and 78 parts of 96% sulphuric acid were slowly added with external cooling to keep the temperature between 20° and 30° C. The mixture was allowed to stand for one-half hour, then poured onto ice, and neutralized with sodium hydroxide solution. The mass was extracted with butanol, the butanol extract separated, and the butanol and water distilled under vacuum from the extract to leave the sulphonated product.

This product was a nearly colorless, waxy substance and had excellent wetting, foaming, and

detergent properties. Further, it was highly resistant to alkaline hydrolysis. For example, a .1% solution of the sulphonated product in a 2% sodium hydroxide showed a wetting time of 8 seconds by the Draves test (see the "American Dyestuff Reporter" vol. 20, p. 201, March 30, 1931, for a description of this test). After boiling for one hour, the wetting time was still 8 seconds, indicating that no substantial portion of the compound had been hydrolyzed. The product was also very soluble in water.

EXAMPLE II

Sulphonated methallyl butyl amide of coconut oil acyl residues

38 grams of a methallyl butyl amine prepared as described above in Example I, page 2, column 2, lines 40 to 48, were dissolved in 400 parts of ethylene dichloride, the solution stirred with cooling on an ice bath to keep the temperature below 10° C., and there were added successively and slowly 39 parts of acid chlorides derived from the mixed acyl residues in coconut oil, 50 parts of aqueous 45% potassium hydroxide and another 39 parts of coconut acid chlorides. The mixture was warmed to 30° C. to coagulate the material insoluble in ethylene dichloride, the ethylene dichloride solution was decanted off, and the solution was dried with anhydrous sodium sulphate. The ethylene dichloride was distilled off to leave the methallyl butyl coconut oil amide as a clear liquid.

32 parts of a methallyl butyl coconut amide obtained as just described were mixed with 13 parts of acetic anhydride, and 17 parts of 96% sulphuric acid were added slowly, with stirring. The mixture was allowed to remain quiescent for ½ hour, then poured onto ice and neutralized with sodium hydroxide. The neutralized mass was extracted with butanol and the butanol distilled off from the extract to leave the sulphonated product. This product had excellent resistance to acid and alkaline hydrolysis, was only slightly inferior to the product of Example I in wetting, foaming and detergent powers, and was readily soluble in water.

EXAMPLE III

Sulphonated methallyl isopropyl lauramide

59 parts of isopropyl amine, 78 parts of alcohol and 45 parts of methallyl chloride were mixed and heated in a closed bottle at 50° C. for 4.5 hours. The mixture was then acidified with aqueous 50% sulphuric acid and distilled on a steam bath and under reduced pressure to remove the alcohol. The remaining solution was made strongly alkaline with potassium hydroxide, and the resultant liberated amine separated, dried by means of solid potassium hydroxide, and fractionally distilled, the methallyl isopropyl amine coming over between 152° and 155° C.

11 parts of a methallyl isopropyl amine prepared as above described were dissolved in 9 parts of pyridine and 10 parts of dioxane. 24 grams of lauric acid chloride were added slowly with external cooling. The mixture was heated on a steam bath for 1 hour, cooled, and extracted with 200 parts of ether. The ether solution was washed successively with 200-part portions of 5% aqueous hydrochloric acid, water, 5% aqueous sodium carbonate and water. The ether was distilled from the solution to leave the methallyl isopropyl lauramide as a colorless liquid.

21 parts of methallyl isopropyl lauramide obtained as above described were mixed with 13 parts of acetic anhydride, and then 18 parts of 96% sulphuric acid were slowly added. The mixture was allowed to stand for one-half hour, then poured onto ice and neutralized with sodium carbonate. The butanol and water were distilled off under vacuum to leave the sulphonated product. This product had excellent wetting, foaming, and detergent properties, and was highly resistant to hydrolysis.

EXAMPLE IV

Sulphonated methallyl myristamide

7 parts of a commercial methallyl amine were dissolved in 8 parts of pyridine and 20 parts of dioxane. 25 grams of myristic acid chloride were added slowly, with external cooling. The mixture was heated on a steam bath for one hour, cooled and extracted with 200 parts of ether. The ether solution was washed successively with 200-part portions of 5% aqueous hydrochloric acid, water, 5% aqueous sodium carbonate, and water. The ether was distilled from the solution to leave the methallyl myristamide as a white solid.

14 parts of methallyl myristamide obtained as above described were mixed with 10 parts of acetic anhydride, and 11 parts of 96% sulphuric acid were slowly added. The mixture was allowed to stand for one-half hour, then poured onto ice. Butanol was added and the mixture was neutralized with sodium carbonate. The butanol and water were distilled off under vacuum to leave the sulphonated product, which was a stiff gummy material, freely soluble in water, possessing excellent wetting and detergent properties and very stable to hydrolysis.

EXAMPLE V

372 parts of aniline, 159 parts of sodium carbonate and 100 parts of water were mixed and refluxed with stirring. 90 parts of methallyl chloride were added over a period of ½ hour. The heating was continued for 4 hours more. Sufficient water was added to dissolve the salts, and the upper layer was separated from the reaction mixture and distilled under 17 mm. pressure through a column. The methallyl phenyl amine distilled between 116° and 122° C.

15 parts of a methallyl phenyl amine obtained as above described were dissolved in 120 parts of ethylene dichloride, the solution was stirred with cooling on an ice bath to keep the temperature below 10° C., and there were added successively and slowly 11 parts of lauric acid chloride, 15 parts of aqueous 45% potassium hydroxide, and another 11 parts of lauric acid chloride. The mixture was warmed to 30° C. to coagulate the material insoluble in ethylene dichloride, and the ethylene dichloride solution was decanted off and dried with anhydrous sodium sulphate. The ethylene dichloride was distilled off to leave the methallyl phenyl lauramide as a clear liquid.

20 parts of 20% oleum were added slowly, with chilling on an ice bath to keep the temperature between 10° and 15° C., to 16 parts of a methallyl phenyl lauramide obtained as above described. The reaction mixture was held between 25° and 30° C. for 15 minutes, and thereafter poured onto ice. The sulphonated product was extracted from the aqueous acid solution by means of bu-

tanol. The butanol extract solution was neutralized with sodium hydroxide solution, then separated from the aqueous solution and subjected to distillation to remove the butanol. The sulphonated product was left as a pale amber material of taffy-like appearance and consistency. This material had the same excellent properties as the products obtained in the other examples. The .1% solution of this material in 2% caustic soda had a Draves' wetting time of 20 seconds, which remained the same after one hour's boiling.

EXAMPLE VI

Methallyl p-tolyl lauramide

65 parts of p-toluidine, 32 parts of sodium carbonate and 75 parts of water were mixed and heated on a steam bath with stirring. 17 parts of methallyl chloride were slowly added and heating continued for 4 hours. Sufficient water was added to dissolve the inorganic salts. The upper layer was separated and fractionally distilled under a pressure of 19 mm. The methallyl p-tolyl amine distilled between 131° and 140° C.

8 parts of a methallyl p-tolyl amine obtained as above described were dissolved in 100 parts of ethylene dichloride, the solution stirred with cooling on an ice bath to keep the temperature below 10° C., and there were added successively and slowly 6 parts of lauric acid chloride, 13 parts of aqueous 45% potassium hydroxide, and another 6 parts of lauric acid chloride. The mixture was warmed to 30° C. to coagulate the material insoluble in ethylene dichloride, the ethylene dichloride solution decanted off and the solution dried with anhydrous sodium sulphate. The ethylene dichloride was distilled off to leave the methallyl p-tolyl lauramide as a clear liquid.

17 parts of methallyl p-tolyl lauramide obtained as just described were mixed with 9 parts of acetic anhydride and there were added slowly, with stirring, 15 parts of 96% sulphuric acid. The mixture was allowed to remain quiescent for ½ hour, then poured onto ice and neutralized with sodium hydroxide. The butanol layer was separated and the butanol distilled off therefrom to leave the sulphonated product. This product had the same excellent properties characterizing the products of the other examples.

A number of other sulphonated amides were made in accordance with this invention and each was tested (1) by means of the Draves' test (see the "American Dyestuff Reporter" vol. 20, page 201, March 30, 1931, for description of this test) at concentrations of .2%, .1% and .05% of the sulphonated amides in water; and (2) by means of a foaming test carried out as follows: 3 gallons of distilled water and 10 cc. of an aqueous 7% solution of calcium chloride were mixed and placed in a cylindrical vessel 13" tall by 11" in diameter. Successive small portions (a 2% solution) of the compound under test were measured out into the vessel, the contents being agitated with a "Lightning" Model C-2 mixer (manufactured by the Manufacturing Equipment Co., Rochester, New York), until a heavy, persistent foam was built up. The number of cc. required of the 2% solution of the material undergoing test was recorded as the foaming number of that material. The results of these tests are tabulated as follows:

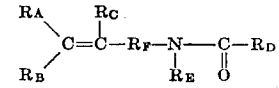
Amide (sulphonated)	Draves' sinking time (seconds at concentration of—)			Foam number (cc. required to produce heavy foam)
	.2%	.1%	.05%	
Methallyl lauramide	37	103	------	
Methallyl methyl lauramide	15	35	------	20.
Methallyl isopropyl lauramide	9	17	------	20.
Methallyl butyl lauramide	6	9	20	5.
Methallyl amyl lauramide	6	11	20	8.
Methallyl 2-ethyl butyl lauramide.	------	10	17	7.
Methallyl secondary hexyl lauramide.	------	15	22	
Methallyl cyclohexyl lauramide.	------	10	22	10.
Methallyl phenyl lauramide	18	28	29	6.
Methallyl 2-ethyl hexyl lauramide.	------	13	29	25.
Methallyl p-tolyl lauramide	12	13	23	9.
Methallyl butyl caprylamide	146	------	------	Fair foamer.
Methallyl butyl capramide	6	37	420	Do.
Methallyl butyl myristamide	36	38	95	12.
Methallyl butyl palmitamide	109	201	------	Fair foamer.
Methallyl butyl amide of coconut oil fatty acids.	14	32	------	7.
Methallyl phenyl capramide	------	15	48	Fair foamer.
Methallyl phenyl amide of coconut oil fatty acids.	------	55	171	8.
Methallyl 2-ethyl hexyl caprylamide.	4	10	55	Fair foamer.
Methallyl 2-ethyl hexyl capramide.	3	8	15	25.
Methallyl 2-ethyl butyl capramide.	------	7	20	Fair foamer.

The expression "sulphonated" when used in connection with the amides of the invention in the claims hereof is to be construed as relating to the sulphonic acid itself, as well as a salt thereof, produced on neutralization of the sulphonic acid group.

Since certain changes in carrying out the above process and certain modifications in the product which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

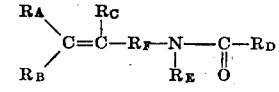
Having described our invention what we claim as new and desire to secure by Letters Patent is:

1. An amide having the general formula:



wherein R_A, R_B and R_C are radicals selected from the group consisting of hydrogen and alkyl groups containing less than 5 carbon atoms, with the proviso that at least one of the double-bonded carbon atoms is attached to 3 other carbon atoms; R_F is an organic linking group containing 1 to 4 carbon atoms; R_D is a fatty acid residue containing between 7 and 29 carbon atoms; and R_E is a radical selected from the group consisting of hydrogen and alkyl, aryl, alphyl and cyclo-aliphatic groups.

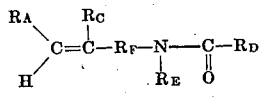
2. An amide having the general formula:



wherein R_A, R_B and R_C are radicals selected from the group consisting of hydrogen and alkyl groups containing less than 5 carbon atoms, with the proviso that at least one of the double-bonded carbon atoms is attached to 3 other carbon atoms and at least one of the radicals R_A, R_B and R_C is a hydrogen atom; R_F is an organic linking group containing 1 to 4 carbon atoms; R_D is a fatty acid

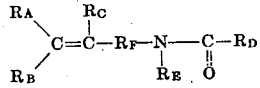
residue containing between 7 and 29 carbon atoms; and R_E is a radical selected from the group consisting of hydrogen and alkyl, aryl, alphyl and cyclo-aliphatic groups.

3. An amide having the general formula:



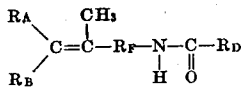
wherein R_A is a radical selected from the group consisting of hydrogen and alkyl groups containing less than 5 carbon atoms; R_C is an alkyl group containing less than 5 carbon atoms; R_F is an organic linking group containing 1 to 4 carbon atoms; R_D is a fatty acid residue containing between 7 and 29 carbon atoms; and R_E is a radical selected from the group consisting of hydrogen and alkyl, aryl, alphyl and cyclo-aliphatic groups.

4. An amide having the general formula:



wherein R_A and R_B are radicals selected from the group consisting of hydrogen and alkyl groups containing less than 5 carbon atoms; R_C is an alkyl group containing less than 5 carbon atoms; R_F is an organic linking group containing 1 to 4 carbon atoms; R_D is a fatty acid residue containing between 7 and 29 carbon atoms; and R_E is a radical selected from the group consisting of hydrogen and alkyl, aryl, alphyl and cyclo-aliphatic groups.

5. An amide having the general formula:



wherein R_A and R_B are radicals selected from the group consisting of hydrogen and alkyl groups containing less than 5 carbon atoms; R_F is an organic linking group containing 1 to 4 carbon atoms; and R_D is a fatty acid residue containing between 7 and 29 carbon atoms.

6. The sulphonation product of an amide having the general formula set forth in claim 1.

7. The sulphonation product of an amide having the general formula set forth in claim 2.

8. The sulphonation product of an amide having the general formula set forth in claim 3.

9. The sulphonation product of an amide having the general formula set forth in claim 4.

10. The sulphonation product of an amide having the general formula set forth in claim 5.

11. Methallyl butyl lauramide.

12. Sulphonated methallyl butyl lauramide.

13. Sulphonated methallyl phenyl lauramide.

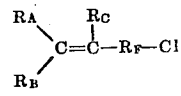
14. The methallyl butyl amide of the fatty aci residues of coconut oil.

15. The sulphonated methallyl butyl amide c the fatty acid residues of coconut oil.

16. A process for the preparation of nov amides, which comprises reacting methallyl chlo ride with a substance selected from the class con sisting of ammonia and primary amines; react ing the resulting amine with an acylating ager containing from 8 to 30 carbon atoms per mole cule to form an amide; and sulphonating th amide.

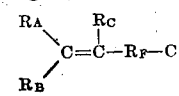
17. A process for the preparation of nov amides, which comprises reacting methallyl chlo ride with a substance selected from the class ammonia and primary amines; and reacting th resulting amine with an acylating agent con taining from 8 to 30 carbon atoms per molecu to form an amide.

18. Process for making an amide which con prises reacting a substance chosen from the cla consisting of ammonia and primary amines wit a compound having the general formula:



wherein R_A, R_B and R_C are radicals selected fro the group consisting of hydrogen and alk groups containing less than 5 carbon atoms, wi the proviso that at least one of the doubl bonded carbon atoms is attached to 3 other ca bon atoms, and R_F is an organic linking gro containing 1 to 4 carbon atoms; and condensi the resulting amine with an acylating compou containing 8 to 30 carbon atoms.

19. Process for making an amide which con prises reacting a substance chosen from the cla consisting of ammonia and primary amines wi a compound having the general formula:



wherein R_A, R_B and R_C are radicals select from the group consisting of hydrogen and all groups containing less than 5 carbon atoms, wi the proviso that at least one of the doub bonded carbon atoms is attached to 3 other ca bon atoms, and R_F is an organic linking gro containing 1 to 4 carbon atoms; condensing t resulting amine with an acylating compound co taining 8 to 30 carbon atoms; and sulphonati the resulting amide.

GIFFORD D. DAVIS
DONALD PRICE.
JOHN G. MILLIGAN