

UNITED STATES PATENT OFFICE

2,306,599

N-ACYLURETHANES AND THEIR
MANUFACTURE

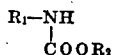
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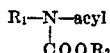
9 Claims. (Cl. 260-295)

This application is a division of our application
Ser. No. 217,019, filed July 1, 1938.

According to the present invention a class of
new, technically valuable compounds is obtained
by treating urethanes of the formula



with fatty acids, their halides, esters and anhy-
drides to form substituted urethanes of the for-
mula



In these formulae R_1 means an aliphatic or hy-
droaromatic radical which may be substituted,
 R_2 means an alkyl, aralkyl, cycloalkyl or aryl
radical which may be substituted or not, and acyl
means the radical of a saturated or unsaturated
carboxylic acid, which may also contain hetero-
atoms or hetero-atom-groupings, such as $-O-$,
 $-S-$, $-N-$, and which may further be sub-
stituted and especially may contain water-solu-
bilizing groups or exchangeable halogen atoms.

For all three substituents, R_1 , R_2 and acyl, the
condition stands that at least one must be an
aliphatic or alicyclic high molecular radical, i. e.,
must contain more than 8 carbon atoms.

The urethanes serving as primary materials
are made in known manner, for instance from
the carboxylic acid amides by Hofmann's decom-
posing process in alcoholic solution or from pri-
mary aliphatic or hydroaromatic amines by de-
composition with appropriate carboxylic acid
derivatives. As examples the following urethanes
may be mentioned:

Undecyl carbamic acid methyl-, ethyl-, propyl-,
butyl-, amyl-ester, heptadecylcarbamic acid
ethyl or amyl ester, urethanes respectively, made
from the carboxylic acids of the naturally oc-
curring or hydrogenated fats or oils, such as for
example palm nut oil fatty acid, coconut oil
fatty acid, soybean oil fatty acid, hydrogenated
cod-liver oil fatty acid or fatty acids of resins or
aliphatic compounds such as naphthenic acid,
carboxylic acids of camphor, of fenchone, methyl
carbamic acid methyl-, butyl-, decyl-, undecyl-,
dodecyl-, octodecyl- and oleic-ester.

Generally all halides, esters and anhydrides of
organic carboxylic acids are adapted for the
acylation of the above named urethanes, such as
for instance acetic, propionic, butyric, stearic,
palmitic, phenoxyacetic, phenyl-amino- and
-thioacetic acid, dodecylthioacetic acid, octyl-
thiopropionic acid and benzoic acid. The car-

boxylic acid derivatives with exchangeable halo-
gen atoms have proved to be of special advantage,
for instance the halides, anhydrides or esters of
 α -halogen fatty acids, such as the mono- and
dichloro-acetic acid, bromosuccinic acid, α -bro-
molauric acid; but aliphatic carboxylic acid de-
rivatives, substituted in other positions by halo-
gen or other organic carboxylic derivatives have
also proved to be quite suitable. As examples
may be mentioned the chlorides of the benzyl-
chloride-4-carboxylic acid, of the 2-chlorobenzoic
acid and its substitution products, such as the
2-chloro-1-benzoic-5-sulphonic acid.

The acylurethanes obtained with the above
mentioned halogenated carboxylic acid deriva-
tives can be used for numerous exchanging reac-
tions due to the exchangeable halogen atoms.
They may for instance be replaced by monova-
lent atom groupings, such as $-OR$, $-SR$, $-NR_2$,
 R generally meaning inorganic and organic sub-
stituents which may be the same or different (if
two are present), as explained fully further on.

The group $-OR$ may be hydroxy, or the radi-
cals of aliphatic, hydroaromatic, aliphatic-aro-
matic or aromatic hydroxy compounds, such as
of methyl-, ethyl-, benzyl-alcohol, cyclo-hexanol,
phenols. The organic hydroxy compounds are
used in the best manner as alkali compounds for
reaction. As examples for this sub-group of the
new acylurethanes are named the reaction prod-
ucts of N-chloraceto-N-undecyl carbamic acid
methylester and sodium phenolate, of N-chlo-
raceto-N-heptadecyl carbamic acid ethyl-ester
and the monosodium salt of glycerol.

The group $-SR$ may be the inorganic radicals
 $-SH$, or radicals of mercaptans. These com-
pounds can be made by decomposition of the
halogen acyl urethanes with alkali-mono- and
-poly-sulphides or the alkali compounds of the
mercaptans. Of the latter compounds may be
named for instance ethyl-, dodecyl-, phenyl-,
benzyl-mercaptan, mercapto acetic acid, α -mer-
capto benzthiazole. As examples for this sub-
group are named the reaction products of N-
chloraceto-N-lauryl carbamic acid methylester
with sodium thiophenolate, sodium sulphhydrate.

Finally, the group $-NR_2$ may be a primary or
secondary amino group. As examples of suit-
able N-compounds for the decomposition are
named ammonia, mono- and di-methyl- or
-ethyl-amine, mono, or diethanolamine, amino-
acetic acid and derivatives, primary and second-
ary aromatic amines such as aniline and substi-
tution products, piperidine and so forth. As ex-
amples for this sub-group of the new acylure-

thanes are enumerated: the reaction products of N-chloraceto-N-heptadecyl carbamic acid alkyl-esters with dimethylamine, diethylamine and so forth.

Compounds being water soluble by virtue of their quaternary N-atoms are easily obtained by the addition of tertiary amines, such as trimethylamine, pyridine, dimethylaniline, triethylamine or by complete alkylation or aralkylation (also with polyoxyethylating agents) of the acylurethane derivatives made with ammonia, primary or secondary amines with esters of low molecular alcohols such as dimethylsulphate.

The new compounds, so far as they are insoluble in water, may be used as softening agents and in the caoutchouc industry. The water soluble new compounds show in aqueous solution distinct properties of capillary activity such as a good foaming, wetting, dispersing and emulsifying power. Certain of the new compounds are also excellent softening agents for cellulose regenerate. Finally some of the new products may be used as bactericidal and fungicidal agents.

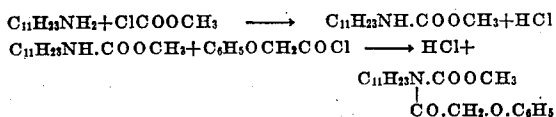
Generally the new acyl urethanes are made by reaction of urethanes in the presence of heat with fatty acid halides or halogen fatty acid halides, if necessary in presence of inert diluents, such as benzene, toluene, xylene. The acylation may also be carried out in presence of acid-binding agents, such as pyridine, diethylaniline etc.

Hereafter some explanatory examples of the process of the present invention are given, without limiting, however, the scope hereinbefore indicated, the parts being by weight.

Example 1

23 parts of undecylcarbamic acid methylester, made for instance by treating undecylamine with chlorocarbonic acid methylester by known method, are dissolved in 100 parts toluene, 19 parts of phenoxyacetic acid chloride are allowed to drop in while stirring and heating to boiling for 12 hours. After working up in known manner, the N-phenoxyaceto-N-undecylcarbamic acid methylester is obtained in form of a semi-solid mass.

The reaction takes place according to the following formulae:

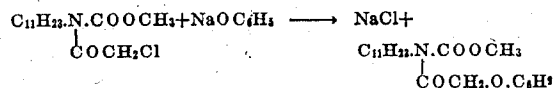
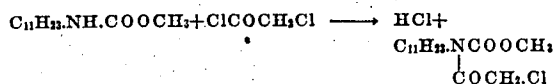


The same compound is obtained by reaction of the N-chloraceto-N-undecylcarbamic acid methylester with phenol.

Example 2

23 parts of undecylcarbamic acid methylester are dissolved in 100 parts of toluene, 13 parts of chloroacetic acid chloride are allowed to drop in whilst vigorously stirring and boiled for 12 hours. After expelling the solvent and the excess of the acid chloride, the N-chloraceto-N-undecyl carbamic acid methylester is obtained in the form of a yellow-brown thick oil. This compound is treated in alcoholic solution with alkali phenolate by heating for 3-4 hours and after working up in the usual manner the N-phenoxy-aceto-N-undecyl-carbamic acid methylester is obtained in form of a semi-solid mass.

The reaction takes place according to the following formulae:

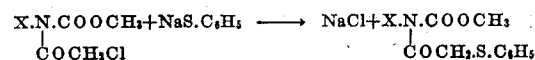


Instead of the aforesaid undecyl-carbamic acid methylester, similar compounds may be used, for example the heptadecyl-carbamic acid ethylester, the undecyl-carbamic acid butylester, as acid chlorides for example butyric acid chloride, propionic acid chloride. The final products show similar properties.

Example 3

11 parts of mercapto benzene are dissolved in 40 parts of alcohol and 4 parts of sodium hydroxide are added. Then 35 parts of the N-chloroacetyl, made from hydrogenated fish oil over the carbamic acid methylester, are added and boiled for 4 hours. On working up in the usual manner, the corresponding N-phenylthioaceto derivative is obtained in form of a semi-solid mass.

The reaction takes place according to the following formulae:



X=hydrocarbon-radical linked with the —COOH-group in hydrogenated fish oil.

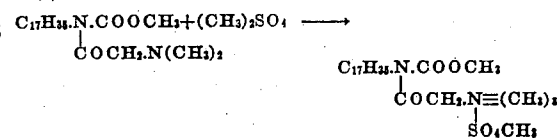
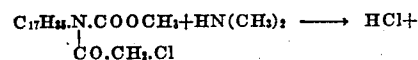
The same compound may also be made on starting with the phenylthioacetic acid chloride.

Example 4

50 parts of N-chloraceto-N-heptadecyl-carbamic acid methylester are allowed to drop into 150 parts of an aqueous solution of dimethylamine of 20.4% strength. At the beginning the reaction mixture becomes slightly hot. After stirring for 24 hours at 60-70° C. the separated oil is isolated, if necessary by shaking out with ether.

15 parts of dimethyl sulphate are added to 38 parts of the obtained N-dimethylaminoaceto-N-heptadecyl carbamic acid methylester and heated for 12 hours on the water bath. A semi-solid, wax-like mass is obtained being easily soluble in water, the solutions of which impart an excellent softness to regenerated and native cellulose.

The reaction takes place according to the following formulae:

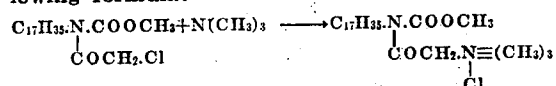


Products with similar properties are obtained with benzylchloride, toluenesulphonic acid esters, also with undecyl carbamic acid methyl and ethyl esters or other compounds mentioned in the general description (page 1, sixth §).

Example 5

30 parts of N-chloraceto-N-heptadecyl carbamic acid methylester are heated with 30 parts of trimethylamine, used in form of an alcoholic solution of 33% strength, with 200 parts of ethyl-alcohol for 5 hours in the autoclave at 130-140° C., then the alcohol and the excess of trimethyl-amine are distilled off. A brown wax-like mass is obtained which is clearly soluble in water.

The reaction takes place according to the following formula:

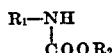


In place of trimethylamine other tertiary amines may be used, such as pyridine, nicotine, triethanolamine.

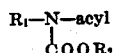
In place of the reaction components used in the above examples, other possibilities of variation may be exercised in very great number by use of the particular compounds as mentioned above in the general description of the specification. There may only be named the reaction of methyl carbamic acid methylester with chlorides of higher fatty acids, such as oleic acid chloride, α -bromolauric acid chloride; the resulting N-acyl-urethanes may be treated in the aforesaid manner, for example with ammonia derivatives and alkylated, if necessary.

What we claim is:

1. A process for the production of N-acyl-urethanes, comprising treating urethanes of the formula



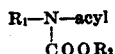
wherein R₁ means one of the group consisting of methyl, undecyl, heptadecyl, of the hydrocarbon radicals connected with the COOH-group in palm nut oil fatty acid, cocoanut oil fatty acid, soyabean oil fatty acid, hydrogenated cod-liver oil fatty acid, resin acid, naphthenic acid, camphor carboxylic acid and fenchone carboxylic acid and R₂ means one of the group consisting of alkyl, benzyl, cycloalkyl and phenyl radicals, with acylating agents to form the N-acyl-urethanes of the following formula:



wherein acyl means the acylradical of a carboxylic acid, whereby at least one of the groups R₁ and R₂ must be one of the group consisting of alkyl and cycloalkyl radicals containing more than 8 carbon atoms.

2. A process for the production of water-soluble N-acylurethanes according to claim 1, wherein the acylating agent contains a water-solubilizing quaternary nitrogen atom.

3. N-acylurethanes of the following formula

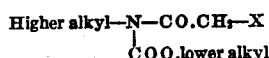


wherein R₁ means one of the group consisting of methyl, undecyl, heptadecyl, of the hydrocarbon

radicals connected with the COOH-group in palm nut oil fatty acid, cocoanut oil fatty acid, soyabean oil fatty acid, hydrogenated cod-liver oil fatty acid, resin acid, naphthenic acid, camphor carboxylic acid and fenchone carboxylic acid and R₂ means one of the group consisting of alkyl, benzyl, cycloalkyl and phenyl radicals, wherein acyl means the acyl radical of a carboxylic acid, whereby at least one of the groups R₁ and R₂ must be one of the group consisting of alkyl and cycloalkyl radicals containing more than 8 carbon atoms, said products being valuable assistants for the textile and related industries.

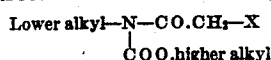
4. N-acylurethanes according to claim 3, whose acyl radicals contain a substituent with a quaternary nitrogen atom.

5. N-acylurethanes of the following formula



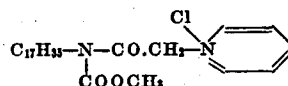
wherein higher alkyl means an alkyl radical having more than 8 carbon atoms and lower alkyl means an alkyl radical with a carbon atom number lower than 8, X being a quaternary-amino group.

6. N-acylurethanes of the following formula



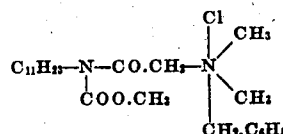
wherein higher alkyl means an alkyl radical having more than 8 carbon atoms and lower alkyl means an alkyl radical with a carbon atom number lower than 8, X being a quaternary-amino group.

7. The acylurethane of the following formula



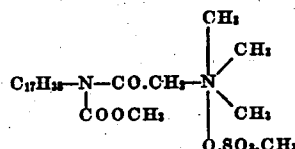
being a semi-solid wax-like mass, easily soluble in water, the solutions of which possess remarkable bactericidal and fungicidal properties.

8. The acylurethane of the following formula



being a semi-solid wax-like mass, easily soluble in water, the solutions of which possess remarkable bactericidal and fungicidal properties.

9. The acylurethane of the following formula



being a semi-solid wax-like mass, easily soluble in water, the solutions of which impart an excellent softness to regenerated and native cellulose.

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