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NEW WATER-REPELLENT AGENT AND
PROCESS OF MAKING SAME

Alfred William Baldwin and Maurice Arthur
Thorold Rogers, Blackley, Manchester, Eng-
land, assignors to Imperial Chemical Industries
Limited, a corporation of Great Britain

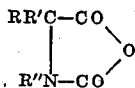
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12, 1940

1 Claim. (Cl. 260—307)

This invention relates to a class of new chemical compounds and to a process of making the same; also to the use of the said compounds for making textile materials water-repellent and to textile materials which have been rendered water-repellent thereby.

It is an object of this invention to provide a class of new chemical compounds which, when applied to textile materials, shall make them water-repellent. A further object is to provide a process for making the said compounds. A further object is to provide water-repellent textiles which shall retain their water-repellency even after subjection to repeated laundering processes or to dry-cleaning treatments. A further object is to provide a process for applying the said compounds to textile materials to achieve this end. Other objects will appear herein-after.

These objects are achieved by the present invention which provides a class of new chemical compounds of the general formula



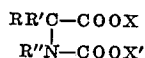
wherein R, R' and R'' are members of the class consisting of hydrogen atoms and monovalent hydrocarbon radicals, and may be alike or different, provided that at least one of them is a monovalent aliphatic hydrocarbon radical of at least 8 carbon atoms.

The new compounds may be regarded as inner anhydrides of α -carboxyamino-carboxylic acids and for some practical purposes this terminology is the most convenient since they are, in fact, readily derived from the α -aminocarboxylic acids of the formula $\text{RR}'\text{C}(\text{NHR}'')-\text{COOH}$, wherein R, R' and R'' have the same meanings as before. They may also be given the more systematic class name of 2:5-diketo-oxazolidines.

As said, the groups R, R' and R'' may be hydrogen atoms or monovalent hydrocarbon radicals; they may be alike or different, but at least one of them must be an aliphatic hydrocarbon radical of at least 8 carbon atoms. The monovalent hydrocarbon radicals may be saturated or unsaturated aliphatic hydrocarbon radicals, cycloaliphatic hydrocarbon radicals or aryl radicals such as phenyl. Thus as representative members of the class of new compounds there may be mentioned, for example, 4-decyl-2:5-diketo-oxazolidine, 4-cetyl-2:5-diketo-oxazolidine, 3-cetyl-4-decyl-2:5-diketo-oxazolidine, 4-methyl-4-heptadecyl-2:5-diketo-oxazolidine,

4:4-diheptadecyl-2:5-diketo-oxazolidine, 3-cyclohexyl-4:4-diheptadecyl-2:5-diketo-oxazolidine, 3-phenyl-4-cetyl-2:5-diketo-oxazolidine, 3-tetradecyl-2:5-diketo-oxazolidine and 4-methyl-4-heptadecenyl-2:5-diketo-oxazolidine.

We make the new 2:5-diketo-oxazolidines by causing a mono-ester of an α -carboxyamino-carboxylic acid of the formula

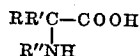


wherein one X is hydrogen and the other is a member of the class consisting of alkyl, cycloalkyl and aralkyl radicals and R, R' and R'' have the same meanings as before, to interact with an agent adapted to convert a carboxylic acid into the corresponding carboxylic acid halide.

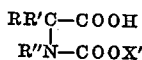
Examples of such agents are the phosphorus halides and oxyhalides, thionyl chloride and phosgene.

The reaction is conveniently brought about by heating the reagents together for a short time at a moderately elevated temperature, for example, 1 hour at 50° C. Inert organic liquids may be present to serve as solvents or diluents if desired but their presence is not necessary. It is usually more convenient to have a diluent present if phosgene is used as a reagent.

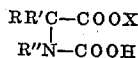
The mono esters of α -carboxyamino-carboxylic acids which are used as starting materials are themselves obtained from the α -aminocarboxylic acids of the formula



If these acids are treated with chloroformic esters, the compounds



are formed. If, on the other hand, they are esterified and the esters are then treated with carbon dioxide in the cold in the manner described in Nature 1939, vol. 144, p. 832, the compounds



are formed. X and X' in these formulae have the same meanings as before.

The α -aminocarboxylic acids which may thus be regarded as the primary starting materials may be made in known manner, for example, by interaction of ammonia or primary amines with α -halogenocarboxylic acids, by treating

the cyanhydrins of appropriate aldehydes and ketones with ammonia or primary amines and subsequently hydrolysing the cyano group of the resulting α -aminonitriles to a carboxyl group or by treating appropriately substituted malonic acids with hydrazoic acid in the manner described in the Journal of the Chemical Society 1939, p. 1564.

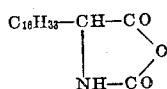
As examples of α -aminocarboxylic acids which, when treated as described above, form compounds suitable to be used as starting materials in the process of the invention there may be mentioned α -aminostearic acid, α -cetylaminolauric acid, α -heptadecylaminolauric acid, α -methyl- α -aminostearic acid, α -methyl- α -aminonondecylic acid, α -cetyl- α -aminostearic acid, α -heptadecyl- α -aminonondecylic acid, α -cetyl- α -cyclohexyl-aminostearic acid, α -heptadecyl- α -cyclohexylaminonondecylic acid, α -phenylaminostearic acid and N-tetradecylglycine.

The new 2:5-diketo-oxazolidines are low melting solids which on heating evolve carbon dioxide and form substances of high molecular weight which are believed to be polyamides.

The more detailed practice of the invention is illustrated by the following examples wherein the parts are given by weight. The invention is not, however, limited to the specific embodiments therein set forth.

Example 1

40 parts of α -carbomethoxyaminostearic acid (of the formula $C_{16}H_{33}.CH(NHCOOCH_3).COOH$, conveniently made from α -aminostearic acid and methyl chloroformate in dioxan solution) and 75 parts of thionyl chloride are heated together for 1 hour at 50° C. The excess of thionyl chloride is then distilled off under sub-atmospheric pressure at 55°-60° C. and the residue is maintained at this temperature for a further half hour. There then remains a solid which is crystallised from light petroleum ether or from chloroform. It then melts at 82°-83° C. with decomposition. This is the new compound anhydro α -carboxyaminostearic acid or 4-cetyl-2:5-diketo-oxazolidine of the formula



It is soluble in warm alcohol and in ether, benzene, petroleum ether, chloroform and ethyl acetate. When heated to 80° C. it gradually decomposes, giving off carbon dioxide and forming a white resin-like substance. The speed of this decomposition reaction increases if the temperature is raised.

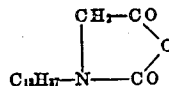
Example 2

30 parts of N-carbomethoxy-N-octadecyl glycine (of the formula



conveniently made by interaction of N-octadecyl glycine with methyl chloroformate) and 50 parts of thionyl chloride are heated together for 1 hour at 35° C. The excess of thionyl chloride is distilled off under sub-atmospheric pressure at 50° C. and the residue is held at the same temperature and pressure for a further hour. There is thus obtained a solid which is crystallised from a mixture of petroleum ether and ethyl acetate. It then has M. P. 68°-70° C. This is the new compound anhydro N-carboxy-N-octadecyl gly-

cine or 3-octadecyl-2:5-diketo-oxazolidine of the formula



It is soluble in benzene, petroleum ether and ethyl acetate. When heated it decomposes, slowly at 100° C. and more rapidly at 130° C., giving off carbon dioxide and forming a substance of a putty-like consistency.

If the thermal decomposition of one of these new diketo-oxazolidines is brought about on a substratum, for example a textile material, then the material is thereby made water-repellent. To achieve this end the diketo-oxazolidine is incorporated with the textile fibres, conveniently by impregnation of the material with a solution of the said compound in an inert organic liquid or with an aqueous emulsion or dispersion of the compound itself or of a solution thereof in an inert water-immiscible organic liquid, and the textile is then dried and heated to bring about the decomposition reaction. It is possible, and, in fact, frequently convenient to merge the drying and heating into one operation. If, however, an aqueous medium is used, it is preferable to separate the two treatments, i. e. to dry the impregnated textile at low temperature, for example, 35°-40° C. and then to raise the temperature, for example to 80°-90° C. to decompose the oxazolidine. Also instead of a single oxazolidine, mixtures of two or more may be used.

It is believed that this decomposition reaction is an intermolecular condensation which results in the elimination of carbon dioxide and the deposition upon and possibly also within the fibres of one or more high molecular polyamides which, it is thought, are the actual water-repellent agents. Nevertheless, the invention is not to be regarded as in any way restricted by this setting forth of a theory to explain the observed facts.

As inert organic liquids suitable to be used in the preparation of solutions of the oxazolidines which are applied to the textiles either as such or after emulsification in an aqueous medium there may be mentioned, for example, benzene, ethylene dichloride or petroleum ether. High-boiling liquids are, in general, to be avoided because of the difficulty of removing them completely from the textile during or after the heating process without either damaging the textile (as for instance by use of unduly high temperatures) or impairing its water-repellence.

The water-repellent finish imparted to textiles in this way is strongly resistant to repeated laundering or dry-cleaning operations.

The textiles treated may be natural or artificial and of animal or vegetable origin. Thus the process may be applied to cotton, wool or silk, regenerated cellulose such as viscose or cuprammonium silk, or cellulose esters or ethers, for example, cellulose acetate.

This feature of the invention is illustrated by the following example, in which the parts are given by weight.

Example 3

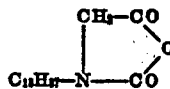
Bleached medium quality plain woven cotton cloth is immersed in a 2% solution of 4-cetyl-2:5-diketo-oxazolidine in benzene, removed, squeezed until it is double its initial weight and then heated for 10 minutes at 90° C. The cloth is thereby made highly water-repellent, the wa-

ter-repellence being resistant to laundering operations and to dry cleaning with benzene or trichloroethylene.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments hereinbefore described, but only as defined in the appended claim.

We claim:

As a new chemical compound 3-octadecyl-2:5-diketo-oxazolidine of the formula



ALFRED WILLIAM BALDWIN.

MAURICE ARTHUR THOROLD ROGERS.