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2,402,526

THIOCYANATE QUATERNARY COMPOUNDS AND METHOD OF PREPARING THE SAME

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No Drawing. Application April 4, 1941, Serial No. 386,845

10 Claims. (Cl. 260—295)

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This application is a continuation-in-part of my copending application Serial No. 363,524, filed October 30, 1940 (Patent No. 2,331,276, issued October 5, 1943). This invention deals with novel organic compounds which may be characterized as being quaternary ammonium thiocyanates containing an acylamido-methylene radical as one substituent of the quaternary N-atom.

It is an object of this invention to provide novel organic compounds which may be useful in the art of treating textile fabric to endow the same with water-repellency characteristics. It is a further object of this invention to provide a process for converting into water-soluble compounds, at least part of the reaction products described and claimed in my parent application above referred to. Other and further important objects of this invention will appear as the description proceeds.

The novel compounds of my present invention are characterized by the general formula

$$R{-}Y{-}\underset{\displaystyle R'}{\overset{\displaystyle |}{N}}{-}CH_2{-}N(tert){-}SCN$$

wherein R is an aliphatic or alicyclic radical containing at least 7 carbon atoms and being free from water-solubilizing groups; Y is a carbonyl link selected from the group consisting of CO, O—CO, NH—CO, CO—NH—CO and O—CO—NH—CO; R′ stands for hydrogen, a lower alkyl group, or a lower alkylene group whose second valency is attached to the nitrogen atom of another radical of the form

$$R{-}Y{-}\overset{\displaystyle |}{N}{-}CH_2{-}N(tert){-}SCN$$

as above defined; and finally, N(tert) stands for the molecule of an aliphatic or heterocyclic tertiary base, for instance pyridine and its homologs, quinoline, trimethylamine, triethylamine, tetramethyl-methylene-diamine, etc.

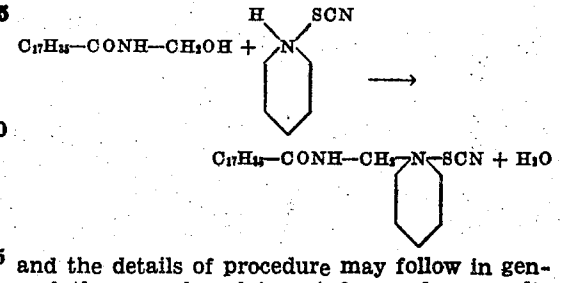
The novel compounds of this invention are of interest in many fields, and have for instance potential utility as insecticides. Their principal value however is in the field of water-proofing textile fiber, inasmuch as I have found these compounds to possess excellent water-repellency endowing qualities without the objection of weakening substantially the strength of the fiber.

Of particular interest in this connection is the subgroup of compounds under the above general formula wherein R—Y jointly represent a simple acyl radical of the form Alk—CO, wherein Alk is an aliphatic hydrocarbon radical, saturated or unsaturated, straight chain or branched chain, but having at least one straight chain of at least 9 carbon atoms.

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The novel compounds are soluble both in organic solvents, for instance benzene or carbontetrachloride, and in water. They are therefore adapted for application to the fiber from either type of bath. As already mentioned, an important quality of the novel compounds when used as water-repellency agents is the absence of tendering of the fiber in the process of baking. Presumably, the thiocyanic acid liberated in the dry heating step is polymerized into harmless by-products which do not attack the fiber as does for instance HCl in certain related agents in common use nowadays. The novel agents may therefore be applied without any buffering or acid absorbing agents which are required in the related compounds.

The quaternary ammonium thiocyanates of this invention may be prepared by reacting an amido methylol compound, for instance, stearamido-methylol, in a basic liquid medium, for instance pyridine, with the thiocyanic acid salt of the chosen tertiary base, for instance pyridine. The reaction then proceeds along lines indicated by the typical equation below:



and the details of procedure may follow in general the procedure laid out for analogous salts in U. S. Patent No. 2,146,392 of Baldwin et al.

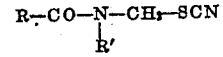
A special process, however, according to this invention is to react the preferred tertiary base, for instance pyridine, upon the fresh reaction products obtained in my parent application above referred to.

These reaction products are themselves prepared, according to my said parent application Serial No. 363,524, by reacting an acylamido-methylene halide with a metal thiocyanate. A typical equation for this reaction is:

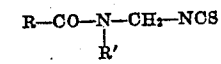
$$R{-}CO{-}\underset{\displaystyle R'}{\overset{\displaystyle |}{N}}{-}CH_2Cl + K{-}SCN \longrightarrow (\text{Reaction product A}) + KCl$$

wherein R and R′ have the same significance as above, while the potassium salt of thiocyanic acid may be replaced by the corresponding sodium, calcium or lead salt, or any other conveniently available form of thiocyanic acid.

"Reaction product A" in the above equation consists presumably of the normal thiocyanate of formula



when fresh. But upon standing it undergoes gradual rearrangement into the isomeric form



therefore, the exact composition of this reaction product is probably a mixture of the two, in a proportion which depends on the age of the reaction product.

The isothiocyanate form does not apparently react with tertiary bases to give quaternary ammonium salts; it is therefore better for the purpose of this invention to react with the selected base upon the fresh reaction product. Alternatively, one may apply this process to a reaction product of any age under the penalty that only part of the same will give the desired quaternary ammonium compound, which however can be separated, if desired, from the unreacted isothiocyanate by making use of their different solubilities in water.

The preferred procedure according to this invention is to mix the reaction product of said parent application with the chosen tertiary base and to let the mixture stand at room temperature for several hours or days. The mixing may be done while the reaction product is in solution in an organic solvent, or after it has been recovered from the solvent. If the chosen tertiary amine is a gas, such as in the case of trimethylamine, the latter may be bubbled into the solution of the thiocyanomethylene reaction compound until 1 mol has been absorbed.

The reaction takes place at room temperature, usually in a few hours, but may be speeded up by warming to 50 to 80° C. for a short time.

The quaternary compounds formed from the thiocyanomethylene reaction product of my said parent application are generally quite soluble in organic solvents like benzene and carbon tetrachloride, and highly concentrated solutions may be prepared in these solvents, containing 50% and more of the quaternary ammonium product. Upon evaporation of the solvent, and occasionally on prolonged standing of the solution, the crystalline quaternary ammonium thiocyanate can be obtained, which dissolves in warm water giving very viscous foaming solutions.

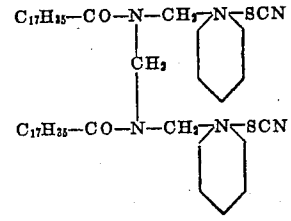
The following examples in which parts by weight are given will serve to illustrate the preferred embodiments of this invention, without however any intent to limit this invention.

Example 1

220 parts of methylene distearamide were converted into the corresponding di-chloromethyl compound by suspending the amide in 800 parts of benzene and then adding in the course of 1½ hours 36 parts of paraformaldehyde while passing in a stream of gaseous hydrogen chloride.

The residue which was obtained upon evaporation was diluted with 50 parts of benzene and added to a suspension of 250 parts of lead thiocyanate in 250 parts of boiling benzene. The lead salt had been previously thoroughly dried by distilling it with benzene. The reaction mixture was kept at the boil for twenty minutes and then cooled to room temperature, decolorized with charcoal and filtered from the inorganic salts and charcoal. The solution thus obtained was still slightly acid to Congo Red paper and was neutralized by agitating the solution with some powdered potassium carbonate, calcium oxide or any other basic compound capable of neutralizing the solution. This solution was mixed with 56 parts of pyridine and allowed to stand at room temperature over night. The originally rather thin solution had changed to a viscous oil. Upon evaporation of the solvent the residue was soluble in water giving a viscous slightly opalescent solution.

The said residue presumably was N,N'-methylene-bis(stearamido-methylene-pyridinium-thiocyanate, of the formula

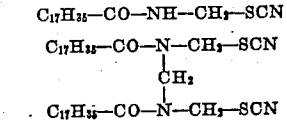


Two solutions of the same were prepared: a 1% solution in water and a 0.5% solution in carbon tetrachloride. Two pieces of cotton were impregnated respectively with the two solutions. Both were air dried, and then heated for five minutes to 150° C. The two pieces were treated for a few minutes in hot water, to wash out the last traces of pyridine and then ironed. Both samples were strongly water-repellent and showed no noticeable tendering of the fiber. Upon washing the two samples with soap and hot water only a very slight decrease in the repellency was observed.

Example 2

180 parts of recrystallized stearic acid amide (containing 95% of the stearic acid radical) were dissolved in 1000 parts of benzene, and then gradually 52 parts of paraformaldehyde were added, while passing in a slow stream of hydrogen chloride gas at 60° C. After a few hours a clear solution results. The water was drawn off and the benzene evaporated in vacuo.

110 parts of this low melting reaction product were dissolved in 100 parts of dry benzene and then 72 parts of lead thiocyanate were added in the course of ten minutes at 70 to 80° C. After all of the lead compound was added the reaction mass was heated for twenty more minutes to 85 to 88° C. Five parts of charcoal were added and the solution was filtered while still warm. The filtrate presumably contained in solution a mixture of thiocyanomethylene compounds of the formulas



and some (more or less) of the corresponding isothiocyanates.

After the solution cooled down to room temperature it was treated for one hour with ten parts of potassium carbonate, filtered again, and then mixed with 100 parts of pyridine.

3% aqueous solutions were prepared from the above product and the following fabrics were

impregnated therewith, then dried, baked, and further treated as in Example 1:

Spun rayon
Rayon crepe
Acetate taffeta
Pure silk
Wool tricotine

In all cases an excellent water repellency was produced. After five washings with soap as in Example 1, the rayon crepe and acetate taffeta had as good repellency as before the washings, while the other three fabrics had lost but very little of their repellency.

Example 3

252 parts of octadecyl carbamate were dissolved in 1600 parts of benzene heated to 60° C. and a stream of hydrogen chloride passed in. To this solution there were added in the course of 1½ hours, 72 grams of paraformaldehyde. When all the formaldehyde had been added the reaction was continued for one hour longer then the aqueous layer drawn off and the benzene solution evaporated in vacuo on the steam bath. The residue, which amounted to 300 parts, contained 11.6% Cl. It was dissolved in 100 parts of benzene and added to 160 parts of dry lead thiocyanate suspended in 300 parts of hot benzene. The reaction mass was kept vigorously boiling for twenty minutes, then filtered while still warm and the filtrate allowed to cool to room temperature and treated with 50 parts of potassium carbamate for 16 hours. Finally the solution was treated with 50 grams of calcium chloride for 5 hours and then filtered from the organic salts. The orange colored residue contained 8.96% sulfur.

A 30% solution of this product in benzene was mixed with half its volume of pyridine and then allowed to stand at room temperature for three days. By this time a considerable amount of a crystalline product separated from the solution. It was filtered off and gave in warm water a very viscous clear solution.

This product is the quaternary pyridinium thiocyanate. The benzene solution obtained from the above filtration was evaporated in vacuo, and the residue obtained dissolved in water to a clear solution. When cotton cloth was impregnated with a 1% aqueous solution of this pyridine compound and heated for a few minutes to 120 to 150° C. a strongly water-repellent material was obtained which was not noticeably impaired by a washing process.

When in the above reaction pyridine was replaced by trimethylamine, a similar reaction occurred. The resulting product had similar properties to the pyridinium compound. It gave clear, viscous solutions in water which decomposed with alkalies and rendered fibrous material water-repellent.

Example 4

280 parts of a commercial mixture of stearic and palmitic acids (approximately 50:50) were converted into the corresponding acid chlorides with thionylchloride. The crude reaction product, which was freed from excess acids by placing the material under vacuum and warming the charge, was dissolved in benzene and then, over a period of one hour, 43 parts of hexamethylene tetramine were added while the charge was heated to 80° C. To the almost clear solution which resulted there were added 228 parts of lead thiocyanate and then again heated to the boil for twenty minutes and then the inorganic salts filtered out. The resulting slightly yellowish solution was neutralized with 30 parts of potassium carbonate and again filtered. Upon evaporation, a low melting hard solid remained which contained essentially one sulfur and two nitrogen atoms per long fatty chain.

The benzene solution obtained above was mixed with 80 parts of pyridine and allowed to stand at room temperature for 24 hours. The viscous solution could be diluted with carbon tetra-chloride or benzene to any desired strength. It had essentially the same properties as the product prepared according to Example 2.

Example 5

282 parts of commercial stearic acid (containing 95% stearic acid) were reacted with 102 parts of phosphorous trichloride and the resulting acid chloride heated for 3 hours on the steam bath while passing under vacuum a slow stream of dry carbon dioxide through the liquid, until all the volatile matter was driven out. The pale yellow oil was diluted with 800 parts of dry benzene, cooled to 0° C. and 44 grams of hexamethylene tetramine added. After stirring for about 1 hour at 0° to 4° C. a clear solution resulted. The reaction product was now heated for 16 hours to 80° C. Then there were added 170 parts of lead thiocyanate and the charge was again heated to the boil for half an hour while distilling out 450 parts of the benzene. The reaction mass was cooled to room temperature and the lead chloride filtered out. To the pale yellow filtrate there were added 70 parts of pyridine and the mixture was allowed to stand at room temperature for two days. The viscous clear solution could be diluted as desired with benzene, carbon tetrachloride, trichloroethylene and other fat solvents. For producing a satisfactory permanent waterproofing and softening effect impregnation of the material with a .5% solution or a .25% solution in carbon tetrachloride was found sufficient.

One may also prepare an aqueous treating bath with the above solution without eliminating the benzene, by diluting the benzene solution with a small amount of acetone and then pouring it into hot water. A slightly opalescent solution is obtained which is quite satisfactory for the impregnation of cellulosic or animal fibers, when it contains .5% to 2% of the active ingredient.

Example 6

100 parts of the thiocyanomethylene compound prepared according to Example 2 were dissolved in 100 parts of benzene and then reacted with 80 parts of triethylamine. After 24 hours the solvent was evaporated. The residue was soluble in water giving foaming viscous solutions.

When applied to cotton in the same way as the corresponding pyridinium compound it gives strongly water-repellent fibers.

In place of triethylamine in the above experiment an equivalent amount of trimethylamine, tetramethyl methylene diamine or tetramethyl ethylene diamine may be used with the same results.

Example 7

150 parts of stearic acid chloride were dissolved in 750 parts of carbon tetrachloride and at 0° C., 22 parts of hexamethylene tetramine added. After agitating for about one hour at 0 to 10° C. the almost clear solution was heated to 80° C. for

16 hours and then 105 parts of lead thiocyanate added. The reaction mass was agitated vigorously for half an hour while a part of the solvent was distilled off. The reaction mass was then cooled to room temperature and filtered. The resulting slightly yellowish, clear solution containing 33% of the active ingredient was reacted with 40 parts of pyridine whereupon a very viscous clear solution was obtained.

Instead of pyridine in the above experiment 25 parts of tetramethylmethylene diamine may be used as a tertiary base. When applied to cellulosic or animal fibers in the same way as outlined in Example 1 good water-repellency is obtained. Instead of stearic acid chloride one may employ in the above example the halides of other acids such as lauric acid, myristic acid, palmitic acid, eicosanoic acid, or acids derived from fish oils having 20 and 22 carbon atoms as well as acids derived from the oxidation of paraffin, hydrogenated rosin acids, or the acids of montan wax.

Example 8

60 parts of methylol stearamide were suspended in 500 parts of pyridine; 55 parts of pyridine thiocyanate were added and the mixture was then heated to 60° C. for 5 hours. On cooling, the clear solution separated a copious amount of a colorless crystalline material, which was filtered off and recrystallized from a mixture of methyl alcohol and ethyl acetate. The crystals which were believed to be the stearamidomethyl pyridinium thiocyanate had a melting point of 76° C. and were soluble in warm water giving very viscous solutions, which could be thinned down by the addition of some alcohol. They were also soluble in organic solvents like benzene or carbon tetrachloride.

When cotton cloth was impregnated with a 0.5% solution of this product in carbon tetrachloride and then air dried and heated for 5 minutes to 150° C., it acquired a high degree of water-repellency. Furthermore, the cloth was not tendered to any detectable extent.

Example 9

165 parts of octadecyl chlorocarbonate

($C_{18}H_{37}$—O—COCl

prepared from octadecyl alcohol and phosgene) were diluted with 750 parts of carbon tetrachloride, then cooled to 0° C., and 22 parts of hexamethylene tetramine were added. After agitating for 1 hour at a temperature of 0 to 10° C., the reaction mixture was heated for 10 hours to 80° C., and then 105 parts of lead thiocyanate were added, while agitating vigorously and distilling off part of the carbon tetrachloride.

The solution is cooled to room temperature and the inorganic salts filtered out.

To the resulting pale yellow solution 40 parts of pyridine were added. After several hours' standing at room temperature, the solution becomes much more viscous and gives with water a foaming milky solution. When applied to cotton at a concentration of 1% and then subjected to a heating treatment the material becomes strongly water repellent.

In a similar manner, quaternary ammonium compounds may be prepared from any of the thiocyanate reaction products mentioned in my parent application above referred to. For instance one may employ the methylene-thiocyanates, prepared according to my said parent application, from the following amides:

Stearamide: $C_{17}H_{35}$—$CONH_2$

Octadecyl-carbamate: $C_{18}H_{37}$—O—$CONH_2$

Octadecyl-urea: $C_{18}H_{37}$—NH—CO—NH_2

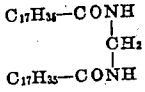
Stearyl-urea: $C_{17}H_{35}$—CONH—$CONH_2$

Octadecyl-allo-phanate:

$C_{18}H_{37}$—O—CONH—$CONH_2$

Methyl-stearamide: $C_{17}H_{35}$—CONH—CH_3

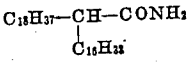
Distearamido-methane:



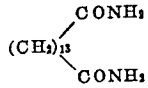
Eicosanoic acid amide: $C_{19}H_{39}CONH_2$

Montanic acid amide: $C_{27}H_{55}$—$CONH_2$

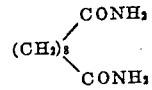
2-hexadecyl-eicosanoic acid amide:



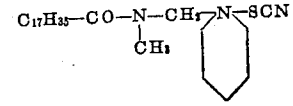
Tridecamethylene-diamide:



Sebacic acid diamide:



In the case of methyl stearamide, when subjected for instance to the process of Example 2 above, the resulting quaternary compound will have the probable formula



As tertiary amines in any of the above examples, heterocyclic tertiary amines like pyridine, quinoline, or the alkyl piperidines may be used, as well as aliphatic tertiary amines like trimethylamine, triethylamine, tetramethyl methylene diamine, tetramethyl ethylene diamine, methyl morpholine, tetramethyl hexamethylene diamine and diethyl cyclohexylamine.

When applied as water-repellents for textile fiber, the novel compounds may be applied by themselves or jointly with other textile finishing agents, for instance, waxes, rubber, synthetic resins, or polymerizable compounds which are soluble in the solvent used for the treatment, and which are generally employed for the purpose of endowing the fabric with resistance to creasing. As such products may be mentioned mono-molecular or polyvinyl acetate, methacrylic esters and ethers of methylol urea. If the product is applied from aqueous solution, it may be applied together with emulsions of waxes, polymerized methacrylic esters polyvinyl acetate, or in the presence of polyvinyl alcohol and partially saponified polyvinyl acetate. Furthermore, it may be applied in the presence of an excess of formaldehyde, under a pH-value sufficiently acid to cause polymerization of the formaldehyde, yielding a crush-resistant pile fabric. (See for instance, Heckert, U. S. P. 2,080,043.)

The said water-repellency treatment of textile fibers may follow in general the details of procedure heretofore employed with other analogous quaternary ammonium compounds (see for instance British Patent Nos. 466,817, 477,991, 493,920; U. S. Patent No. 2,160,176 and copending

application of Bacon, Serial No. 336,375 which issued August 17, 1943, as Patent No. 2,327,160); and may be applied to textile material of vegetable, animal or artificial origin, for instance, cotton, regenerated cellulose, cellulose acetate, wool, silk, nylon; and also to non-textile fibers, for instance leather, paper or transparent cellulosic film.

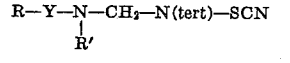
The novel reagents of this invention may be applied to the fabric from either aqueous or organic solution, and have the advantage over quaternary ammonium compounds heretofore employed for this purpose in that they give a high degree of water-repellency without tendering the fiber. The weakening of the fiber by the acid liberated in the "baking" step (heating the impregnated fiber in the absence of moisture) constituted a source of annoyance to the trade heretofore. Attempts have been made to solve the problem by adding buffers to the impregnation baths or by replacing the anion in such compounds as stearamido-methyl pyridinium chloride by anions of weak acids such as acetic, lactic, salicylic, glycollic or phthalic (U. S. Patent Nos. 2,160,176 and 2,210,442). It seems, however, that the quaternary salts of these weaker acids did not give such good water-repellency as the quaternary ammonium chlorides.

The reagents of the present invention combine high water-repellency with safety to fiber and thus solve the above noxious problem of tendering without recourse to buffers. Nevertheless buffers may be employed with my novel agents if desired.

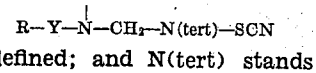
It will be understood that my invention is susceptible of wide variation in the details thereof without departing from the spirit of this invention, as defined by the subjoined claims:

I claim:

1. Quaternary ammonium compounds of the general formula

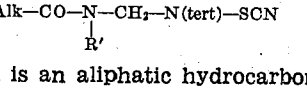


wherein R is a member of the group consisting of aliphatic and alicyclic radicals containing at least 7 carbon atoms and being free from water-solubilizing groups; Y is a carbonyl link selected from the group consisting of CO, O—CO, NH—CO, CO—NH—CO and O—CO—NH—CO; R′ stands for a member of the group consisting of hydrogen, a lower alkyl group, and a lower alkylene group whose second valency is attached to the nitrogen atom of another radical of the form

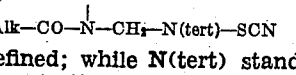


as above defined; and N(tert) stands for the molecule of a tertiary base selected from the group consisting of aliphatic and heterocyclic tertiary nitrogenous bases.

2. A compound of the general formula

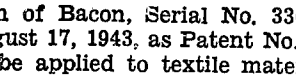


wherein Alk is an aliphatic hydrocarbon radical having at least 9 carbon atoms; R′ stands for a member of the group consisting of hydrogen, a lower alkyl and a lower alkylene whose other valency is attached to the nitrogen atom of a similar radical of the form



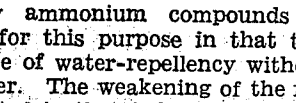
as herein defined; while N(tert) stands for the molecule of a tertiary base selected from the group consisting of aliphatic and heterocyclic tertiary nitrogenous bases.

3. A compound of the general formula



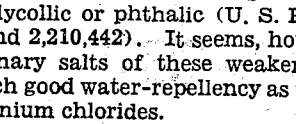
wherein Alk stands for an aliphatic hydrocarbon radical having at least 9 carbon atoms while N(tert) stands for the molecule of a tertiary base selected from the group consisting of aliphatic and heterocyclic tertiary nitrogenous bases.

4. A compound of the general formula

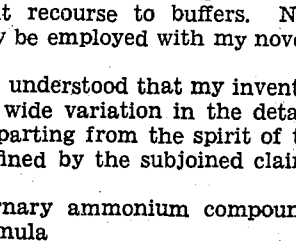


wherein Alk stands for an aliphatic hydrocarbon radical having at least 9 carbon atoms while N(tert) stands for the molecule of a tertiary base selected from the group consisting of aliphatic and heterocyclic tertiary nitrogenous bases.

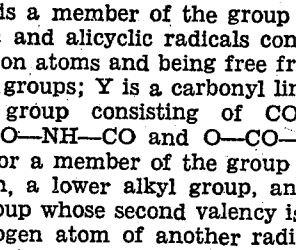
5. Stearamido-methyl-pyridinium thiocyanate, being the compound of the formula



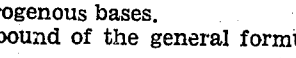
6. N,N′-methylene-bis(stearamido-methyl-pyridinium thiocyanate), being the compound represented by the formula



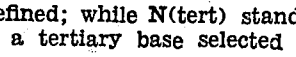
7. N,N′-methylene-bis(octadecoxy-carbamido-methylene-pyridinium thiocyanate), being the compound represented by the formula



8. The process of preparing novel water-soluble organic compounds useful in the field of waterproofing textile fiber, which comprises reacting with a tertiary base upon the reaction product of a metal thiocyanate with a methylene halide compound of the general formula



wherein R stands for an aliphatic or alicyclic radical containing at least 7 carbon atoms and being free from water-solubilizing groups; Y is a carbonyl group selected from the group consisting of CO, O—CO, NH—CO, CO—NH—CO and O—CO—NH—CO; X is halogen; while R′ stands for a member of the group consisting of hydrogen, a lower alkyl, and a lower alkylene whose other valency is attached to the nitrogen atom of another radical of the form



as herein defined.

9. The process of preparing novel water-soluble organic compounds useful in the field of waterproofing textile fiber, which comprises reacting with a tertiary base upon a methylene thiocyanate compound of the formula

$$Alk—CO—NH—CH_2—SCN$$

wherein Alk is an aliphatic hydrocarbon radical having at least 9 carbon atoms.

10. The process of preparing novel water-soluble organic compounds useful in the field of

waterproofing textile fiber, which comprises reacting with a tertiary base upon a methylene thiocyanate compound of the formula

$$\begin{array}{l} Alk—CO—N—CH_2—SCN \\ \qquad\qquad\quad | \\ \qquad\qquad CH_2 \\ \qquad\qquad\quad | \\ Alk—CO—N—CH_2—SCN \end{array}$$

wherein Alk is an aliphatic hydrocarbon radical having at least 9 carbon atoms.

JOSEF PIKL.