

ALIEN PROPERTY CUSTODIAN

CONDENSATION PRODUCTS

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vested in the Alien Property Custodian

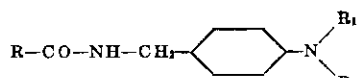
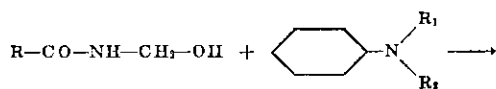
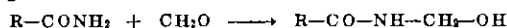
No Drawing. Application filed July 15, 1939

My invention relates to new condensation products and a method of manufacturing the same. It especially relates to compounds, in which an organic acid amide is connected with a tertiary aromatic amine by the CH_2 -group. Such products are made by reacting the methylol-compound of an organic acid amide with a tertiary aromatic amine in which the p-position to the amino-group is free from substituents.

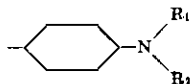
According to my invention these compounds or their salts with various acids are especially valuable as wetting agents, emulsifying agents and for different textile purposes. They have also valuable qualities as bactericidal and fungicidal agents.

I have further found that the new condensation products are of great value in the form of their quaternary addition products which are made by treating them with esters of strong acids, e. g. dimethylsulphate, diethylsulphate and other alkyl-esters of sulphuric acid, alkyl-esters of sulphonic acids like benzene- and toluene-sulphonic acid, the alkyl- or aralkyl-esters of hydrochloric, hydrobromic and hydroiodic acid etc.

As I have found the condensation of methylol-amides and tertiary aromatic amines can be effected with a good yield according to the following formulae:



that means a tertiary aromatic amine of the formula

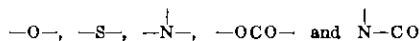


in which the p-position to the group



has no substituents, is treated with methylol-derivatives of primary acid amides of the formula $\text{R}-\text{CO}-\text{NH}_2$. R_1 and R_2 stand for alkyl- and aralkyl- and R stands for the residue of a hydrocarbon taken from the class of aliphatic, aromatic and aliphatic-aromatic hydrocarbons.

The residue of the aliphatic hydrocarbon comprises chains formed merely of carbon atoms and chains formed of carbon atoms interrupted by links comprising

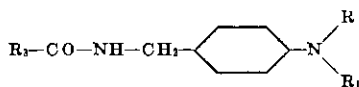


The condensation occurs in the presence of catalysts of acid character able to split off or to bind chemically water, for instance mineral acids, like sulphuric acid, hydrochloric acid, phosphoric acid, salts with acid reaction like zinc-chloride, aluminium-chloride or homopolar compounds like the halogenides of phosphorus, the reaction products of which have an acid nature. Besides other substances combining with water may be present, e. g. acid anhydrides like acetic anhydride. As the catalysts of strong acid character, especially mineral acids, may react with the tertiary aromatic amine to form a stable mineral acid salt, it is necessary to use an excess of the amine over the stoichiometric ratio, so that at least one mol of the amine be present in the free form. Generally it may be favorable to use a further excess of the organic base over the lowest ratio which has been calculated, for sometimes a small quantity of formaldehyde, which may be split off from the methylol amide, reacts with the tertiary amine. As it is known, one mol of formaldehyde may combine with two moles of the tertiary amine forming, for instance, tetraalkyldiaminodiphenylmethane. In consequence of this reaction a respective quantity of the amine is chemically bound and therefore is not available for further reaction.

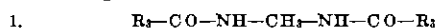
Amides which may be used for the present process are the following, though my invention is not limited to them: the amides of capronic acid, caprylic, capric, lauric, myristic, palmitic, stearic, oleic acid, amides of other natural or artificial fatty acids, or amides of alkylated glycolic or thioglycolic acid, which may be obtained by treating fatty alcohols or mercaptans with chloracetic acid, or amides of amino-acidamides. Other examples of amides are the amides of aromatic carbonic acids, of arylacetic acids, of aryl-oxy-acetic acids, the latter being prepared from phenols and chloracetic acid and many others. The tertiary aromatic amines used in the present process are for instance dimethylaniline, diethylaniline, dipropylaniline, methylbenzylaniline and other symmetric or asymmetric compounds of similar character, N-dialkyl-m-toluidines, N-dialkyl-o-aminophenols or the respective m- or p-compounds or the alkyl- or

aryl-ethers of the same. One may also start from the respective compounds of the naphthalene-, diphenyl- or diphenylmethane series. The reaction may be advantageously accelerated by raising the temperature to about 50–150°. Solvents which are indifferent to the components of the reaction may be present.

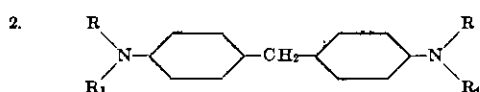
The condensation-process runs in the first line forming compounds of the formula



which are soluble in diluted acids. Besides by-products may be forced, f. i. the following methylene compounds of the starting materials:



and



Generally only very small amounts of these methylene-compounds are formed. The compounds according to formula I may be condensed in the same process with the aromatic amine or fresh such amine may be added. In this case one mole of the respective amide is split off and a further condensation takes place. The by-products may be easily removed. The compound (I) may be separated as it is not soluble in diluted acids. On the contrary the substituted diamino-diphenylmethane (II) is especially soluble in weak acids, f. i. in a 5–10% acetic acid and it may be easily removed in this manner or it may be removed as it can not be separated out of its solution in mineral acids by the addition of salt.

The compounds which are obtained by the present process are solid or fluid or oil-like substances. They are readily and clearly soluble in diluted mineral acids, like 5% hydrochloric acid, forming solutions with great foaming power. They may be readily precipitated from the acid solutions by adding alkalis or an alkaline salt yielding the free compounds. By the addition of neutral salts the new compounds may be precipitated in the form of salts. By treating the condensation products with esters of strong acids, like dialkylsulphate, they may be transformed into the quaternary ammonium compounds. These quaternary compounds as well as the condensation products themselves may be used as emulsifying, equalizing and wetting agents. They are well suited for textile and colouring purposes and for treating natural and artificial fibres. They may also be used in the manufacture of pharmaceuticals. As they have strong bactericidal and fungicidal power they may be used as preserving, disinfecting agents and for combatting insects and plant-diseases.

My process may be characterized by the following examples:

Example 1

	Parts
Capriacid-methylolamide.....	10
Diethylaniline.....	30
Zinc-chloride.....	5

are well stirred at ordinary temperature till all methylolamide has reacted. The excess of diethylaniline is removed by vapour distillation. The residue is soluble for its greatest part in 5% hydrochloric acid, non-basic reaction products being separated from it by extraction with ether.

The products of basic character may be precipitated by addition of alkali. They are dissolved in ether and removed from the p-p'-tetraethyl-diaminodiphenylmethane which has been formed as a by-product by repeatedly shaking the ether with 10% acetic acid. The condensation product is obtained in a very good yield. It is a light yellow oil, which is readily soluble in diluted mineral acids, yielding a strongly foaming solution. By treating the new compound with 1 mol of dimethylsulphate the quaternary compound is formed, the solution of which is stable when treated with diluted alkalis.

Example 2

The methylolamide of lauric acid.....	10
Dimethylaniline.....	20
Acetic acid.....	20
Zinc-chloride.....	10

are shaken during 20 hours at a temperature of 60°. The reaction product is treated with vapour and the residue is dissolved in a 5% hydrochloric acid. The solution is freed from insoluble by-products by treating it with ether. The hydrochloric acid solution is treated with the equal volume of a saturated solution of common salt. A small quantity of ether is added. The reaction product separates as a fluid intermediate layer between the aqueous solution and the ether. By repeating this precipitation process the new compound is obtained in a pure state. It is a light yellow oil which is readily soluble in diluted mineral acids and has pronounced foaming and wetting power.

Example 3

A mixture of the acids of cocoanut oil is distilled in vacuo, transformed into the chlorides and transformed into the amides by treating with ammonia. 40 parts of this amide are dissolved in 40 parts by volume of toluene at a temperature of about 80°. The solution is shaken for half an hour with one part of dry potassium carbonate and 6.5 parts of paraformaldehyde. The solution is then decanted from the carbonate and mixed with 9.5 parts of concentrated sulphuric acid and 75 parts of diethylaniline at a temperature of 80°. The mixture is shaken for 20–40 hours at a temperature of 80° and the reaction product is neutralized with ammonia and freed from an excess of diethylaniline and toluene by vapour-distillation. The residue, which has a semisolid character, is dissolved in ether, about 3–4 parts remaining insoluble. The solution is extracted with 5% hydrochloric acid. The non-basic by-products remain in the ether. The acid solution is shaken with an equal volume of saturated sodium chloride solution and a small quantity of ether. Upon standing for a while several layers are formed, the intermediate layer containing the new condensation product. This layer is treated two times with equal parts of 5% hydrochloric acid and saturated sodium chloride solution. Now the basic condensation product is precipitated. Its ethereal solution is decolorized with charcoal and evaporated. The residue consists of 40 parts of a light-yellow oil, which is clearly soluble in diluted hydrochloric acid.

Example 4

40 parts of the amide of cocoanut oil-fatty-acids, which has been prepared as it is shown in Example 3, is treated with formaldehyde, as it is described there. The product which has been decanted from the potassium carbonate is shaken

for 10 hours with 9.5 parts of concentrated sulphuric acid and 70 parts of dimethylaniline at a temperature of 80°, and then shaken for 20 hours at a temperature of 110°. The reaction mass is treated according the Example 1. A light-yellow oil is obtained in a very good yield. By treating this oil with dimethylsulphate a quaternary compound is obtained, which in the pure state is an almost colorless resin, which easily dissolves in water with neutral reaction. It is very stable when treated with acids or alkalis.

Example 5

40 parts of the amide of cocoa-nut-fatty acids are dissolved in 200 parts by volume of hot 50% hydrochloric acid, treated with 8.5 parts of 40% formaldehyde solution and heated for 2 hours on the vapour bath. The cooled mass is freed from hydrochloric acid by washing with water and dried. 42 parts of methylenedifatty acid amide are obtained. The dry product is heated with 60 parts of diethylaniline and 9.5 parts of concentrated sulphuric acid to about 150° for 20 hours in an atmosphere of carbon dioxide. The mass is well stirred and treated according to Example 3. The same product as described in Example 3 is obtained in a good yield.

Example 6

Cocoa-nut-oil-fatty acids are distilled in vacuo and the fraction of boiling point about 140–200° at 10 mm. is transformed into the amide by heating it with ammonia. 400 parts of this amide are dissolved in 400 parts by volume of benzene and treated for an hour with 70 parts of paraform-

aldehyde, and 10 parts of potassium carbonate, the temperature being about 80°. To the methylol-compound which has been formed, 800 parts of dimethylaniline are added and then 300 parts of acetic acid anhydride are dropped into the mass, the temperature being kept at 80–85°. The condensation process is completed by slowly adding 50 parts of concentrated sulphuric acid in about one hour. After about 2–3 hours' heating at 80° the condensation is finished. In order to remove by-products and an excess of dimethylaniline the reaction product is dissolved in 2000 parts by volume of benzene and extracted five times with a mixture of 2000 parts of concentrated sodium chloride solution, 660 parts of concentrated hydrochloric acid, 1240 parts of water and 300 parts of acetic acid, all these parts being by volume. Upon standing the solution separates into two layers. Each time the bottom layer is separated off and 550 parts of dimethylaniline may be obtained from the united separated layers. The upper layer of benzene is alkalinized by adding 400 parts by volume of a 40% sodium hydroxide solution. The aqueous layer is removed and the benzene solution is dried with potassium carbonate. When the benzene is distilled off, an almost colorless waxy residue is obtained in an amount of 560–570 parts (about 85% of the theoretical yield). 1000 parts of this residue are treated at about 130° with 760 parts of the methylester of p-toluene-sulphonic acid for 5 hours. A waxy yellow mass is formed in quantitative yield, which is clearly soluble in water.

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