

## UNITED STATES PATENT OFFICE

2,519,924

ALKYL DIMETHYL BENZYL AMMONIUM  
NAPHTHENATEMilton Nowak, Brooklyn, N. Y., assignor to Nuo-  
dex Products Co., Inc., Elizabeth, N. J., a cor-  
poration of New YorkNo Drawing. Application November 7, 1946,  
Serial No. 708,445

2 Claims. (Cl. 260-404)

1

This invention is an agent useful for pest control and for immunizing articles of commerce against the ravages of destructive macro and micro-organisms, such as bacteria, fungi, insects, various forms of marine life, etc.

Heretofore certain agents, variously known as toxicants, pest control agents, or fungicides have been widely employed. Such agents have, however, lacked certain important characteristics which limited either or both their utility and scope of application. For example, cellulosic fabrics, particularly cotton fabrics, when exposed to the weather, commonly suffer from the attacks of cellulose destroying fungi. When attempts were made in the past to protect such fabrics by known pest control agents, certain difficulties were encountered. Fungicides have commonly been used in this connection, but they have been of such relatively low activity that relatively high percentages of them were needed to protect the fabric, and, in many instances, such protection resulted in undesirable coloring of such fabric. Still others lacked chemical stability and decomposed as the fabric aged, particularly when exposed to the weather. Not uncommonly this decomposition has been accompanied by an ancillary reaction causing chemical degradation of the fabric which it was desired to protect. The protection of fabrics destined for outdoor use against fungus attack without imparting undesirable characteristics to the fabric has constituted a real problem in the past.

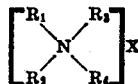
These and other weaknesses of known fungus and pest control agents have prompted me to carry out extended research work and experimentation in an effort to develop a better protective agent which would be devoid of the disadvantages to which I have referred and others.

As a result of this protracted research and investigation, a certain group of chemical compounds has been produced which are found to be ideally suited as pest control agents adapted for a wide variety of uses, particularly as immunizing or pest control agents against fungi and bacteria. These compounds are oil-soluble quaternary ammonium compounds and more particularly quaternary ammonium salts. By "quaternary ammonium salts" is meant those substituted ammonium salts wherein the four valences

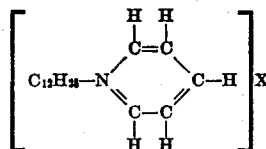
2

of nitrogen are linked to organic radicals, while the fifth valence is linked to an anion.

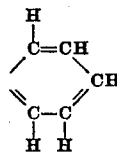
These compounds are characterized by the following structural formula:



where: X represents a substantially water-insoluble and oil-soluble acid and  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are organic radicals, either aliphatic, alicyclic, aromatic, or heterocyclic and may be substituted or unsubstituted. The four radicals  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  may be identical as in tetramethyl ammonium bromide, or completely dissimilar, as in cetylmethylbenzyl ammonium chloride. In addition, two or three of the radicals,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , may be replaced by a ring structure of equivalent valence as in lauryl pyridinium naphthenate



where three groups are replaced by the trivalent ring structure



and X is naphthenic acid, which is a substantially water-insoluble and oil-soluble organic acid.

Among examples of the quaternary ammonium compounds of this invention are:

Dodecyl dimethyl benzyl ammonium naphthenate  
Lauryl pyridinium naphthenate

Alkyl dimethyl benzyl ammonium naphthenate

45 Alkyl dimethyl benzyl ammonium oleate

Lauryl pyridinium oleate

9-octadecenyl dimethyl ethyl ammonium naphthenate

9-octadecenyl dimethyl ethyl ammonium oleate

50 Cetyl dimethyl benzyl ammonium naphthenate

Cetyl dimethyl benzyl ammonium oleate  
 Cetyl dimethyl benzyl ammonium 2-ethyl hexo-  
 ate  
 Cetyl dimethyl benzyl ammonium tallate  
 Cetyl dimethyl benzyl ammonium alkyl sulfonate  
 9-octadecenyl dimethyl ethyl ammonium 2-ethyl-  
 hexoate  
 9-octadecenyl dimethyl ethyl ammonium tallate  
 9-octadecenyl dimethyl ethyl ammonium alkyl  
 sulfonate  
 Alkyl dimethyl benzyl ammonium 2-ethylhexoate  
 Alkyl dimethyl benzyl ammonium tallate  
 Alkyl dimethyl benzyl ammonium alkyl sulfonate  
 Lauryl pyridinium 2-ethylhexoate  
 Lauryl pyridinium tallate  
 Lauryl pyridinium alkyl sulfonate  
 Tetraethyl ammonium naphthenate  
 Dimethyl ethyl propyl ammonium naphthenate  
 Lauryl pyridinium naphthenate 2-ethylhexoate  
 combination  
 Lauryl pyridinium naphthenate dodecyl dimethyl  
 benzyl ammonium naphthenate combination  
 Alkyl dimethyl benzyl ammonium laurate  
 Alkyl dimethyl benzyl ammonium linoleate  
 Didodecyl dimethyl ammonium naphthenate  
 Dodecyl dimethyl benzyl ammonium mono-octyl  
 phthalate  
 Dodecyl dimethyl-o-chlorobenzyl ammonium li-  
 noleate  
 Di-isobutylphenoxyethoxyethyl dimethyl benzyl  
 ammonium 2-ethylhexoate  
 Lauryl pyridinium-p-tert.-amylphenoxyacetate  
 p-Tert.-octylphenoxyethoxyethyl dimethyl benzyl  
 ammonium oleate  
 N-(lauric acid ester of colamino-formyl methyl)  
 dimethyl benzyl ammonium naphthenate  
 Dodecyl dimethyl benzyl ammonium laurate.

Exhaustive researches in the production of the quaternary ammonium salts of this invention have been carried out in connection with a great number of acids (represented by X in the structural formula) and it has been found that all the many water-insoluble and oil-soluble acids tested were operative in the carrying out of this invention. In fact no oil-soluble and water-insoluble organic acid has been found which is inoperative and the tests therefore proved that all oil-soluble and water-insoluble organic acids will function satisfactorily in the production of the novel chemical compound of this invention and all compounds thus produced are oil-soluble and substantially water-insoluble.

These compounds may be prepared by a number of different methods. They may be obtained as the pure compounds, but it is also practical to prepare these in the form of solutions in various organic solvents, including benzene. They may also be prepared in other vehicles in which they may be soluble, such as synthetic resin solutions, etc.

The following examples are illustrative of the present invention.

**Example 1.—Preparation of dodecyl dimethyl benzyl ammonium naphthenate**

170 grams (.25 M) of 50% dodecyl dimethyl benzyl ammonium chloride are dissolved in 500 grams ethyl alcohol and heated with agitation to 60° C. A soap is then prepared consisting of 20 grams of a 50% solution of sodium hydroxide, dissolved in 300 grams of ethyl alcohol to which has been added 55.9 grams (.25 M) of naphthenic acid (acid number 251). The soap should test acid to phenolphthalein. This soap is added slowly, under agitation, to the previously pre-

pared solution of dodecyl dimethyl benzyl ammonium chloride and the resulting solution is stripped of alcohol and water "in vacuo" at a bath temperature of 100° C. The resulting product is a brown viscous liquid which should be filtered through a steam funnel to remove the precipitated sodium chloride of which 14 grams (.25 M) is recovered. The resulting dodecyl dimethyl benzyl ammonium naphthenate is soluble in benzol, toluol, mineral spirits, mineral oil, linseed oil and all the common fat solvents.

**Example 2.—Preparation of mixed alkyl dimethyl benzyl ammonium naphthenate (70% solution)**

736 grams (1 M) of 50% mixed alkyl dimethyl benzyl ammonium chloride (derived from amines obtained from coconut fatty acids and indicating a mixture of alkyl chains such as occur in coconut oil and averaging 12 carbon atoms in length), are added to a previously prepared soap solution consisting of 40 grams (1 M) of sodium hydroxide, 200 grams of water and 247 grams of naphthenic acid (acid number 228). This soap should test acid to phenolphthalein. The resulting solution is stripped of water and alcohol "in vacuo" at a bath temperature of 100° C. When dry, 242 grams of "Cellosolve" (ethylene glycol monoethyl ether) or alcohol (ethyl) are added and the resulting solution filtered. 58 grams of sodium chloride are recovered and the end product is a free flowing light amber liquid, soluble in xylol, mineral oil, linseed oil and the common fat solvents.

**Example 3.—Preparation of 9-octadecenyl dimethyl ethyl ammonium naphthenate**

134 grams (.25 M) of 75% 9-octadecenyl dimethyl ethyl ammonium bromide are dissolved in 500 grams of ethyl alcohol and heated with agitation to 60° C. A soap is then prepared consisting of 28 grams of a 50% aqueous solution of potassium hydroxide dissolved in 300 grams of ethyl alcohol, to which has been added 55.9 grams (.25 M) of naphthenic acid (acid number 251). The soap should test acid to phenolphthalein. This soap is added slowly, under agitation, to the previously prepared solution of 9-octadecenyl dimethyl ethyl ammonium bromide and the resulting mixture is stripped of alcohol and water under water vacuum at a bath temperature of 100° C. The resulting product is an amber viscous liquid requiring filtration through a steam funnel to remove the precipitated potassium bromide of which 29.7 grams is recovered. The 9-octadecenyl dimethyl ethyl ammonium naphthenate is soluble in benzol, toluol, mineral spirits, mineral oil, linseed oil and all the common fat solvents.

**Example 4.—Preparation of cetyl dimethyl benzyl ammonium naphthenate**

381.5 grams (.25 M) of 25% cetyl dimethyl benzyl ammonium chloride are dissolved in 500 grams of ethyl alcohol and heated with agitation to 60° C. A soap is then prepared consisting of 20 grams of a 50% aqueous solution of sodium hydroxide dissolved in 300 grams of ethyl alcohol to which is added 55.9 grams (.25 M) of naphthenic acid (acid number 251). The soap should test acid to phenolphthalein. This soap is added slowly under agitation to the previously prepared solution of cetyl dimethyl benzyl ammonium chloride and the resulting mixture is stripped of alcohol and water under vacuum at a bath temperature of 100° C. The product is an amber

5

viscous liquid requiring filtration through a steam funnel to remove the precipitated sodium chloride, of which 14 grams (.25 M) are recovered. The product is soluble in benzol, toluol, mineral spirits, mineral oil, linseed oil and all the common fat solvents.

In a similar manner a plurality of quaternary raw materials may be reacted with a plurality of acids within the purview of this invention.

The end products of the foregoing examples may be used in practice in solution or otherwise as the fungicidal agent. However, these fungicidal agents may be used in combinations, such, for example, as combinations of such quaternary compounds plus other fungicidal agents, such as metallic naphthenates, oleates, tallates, or the like.

In the majority of examples hereinbefore given it has been shown how the end products may be made by reacting water-soluble quaternary ammonium salts with a sodium or potassium salt of a water-insoluble organic acid to obtain the end products. The preparation of the water-soluble quaternary ammonium compound itself may be carried out in accordance with a number of well known conventional methods.

In other examples given, the end product has been made by reacting together the water-insoluble organic acid with the water-soluble hydroxide of the quaternary ammonium compound. Such hydroxide quaternary ammonium compounds may likewise be prepared by conventional methods. It is to be understood further that the preparation of the end products of this invention are not necessarily limited to the process steps given in the examples which have been advanced for the purpose of illustration.

The compounds prepared in accordance with this invention have been shown by tests to be highly effective as pest control agents. For example, the compound made according to Example 1 was applied on a typical awning fabric (10 oz. duck). It was applied in various concentrations ranging from as little as .25% to 20% per weight of fabric. These various treated fabric specimens together with an untreated fabric specimen control were exposed to many different conditions among them weathering, burial in composted soil rich in micro-organisms, exposed in a high humidity room favoring mildew growth, etc. It was found that even the presence of as little as .25% of this composition already had a discernible effect upon the resistance of the fabric to rotting and mildew which are caused by fungi. At the levels of 1% and higher, the treated fabric remained unaffected by the fungi activities even when exposed to them for as long as six months. The untreated fabric by comparison lost its tensile strength entirely upon two weeks exposure to the soil and it lost substantially all of its strength when exposed to high humidity for two months. There was no secondary chemical effect of this compound upon the fabric; that is, the treated fabric did not suffer chemically from the compound even when exposed to the weather for as long as six months.

In another series of tests, a number of the compounds enumerated in the various examples above

6

were investigated as pest control agents in connection with economic crops. For this purpose they were applied in the form of their aqueous emulsions and they were also applied after first being diluted with inert carriers, such as bentonite clays. The preliminary results show great promise for their performance as pest control agents in the field of economic crops. In still another test, the compounds described in the various examples were checked for their effectiveness in coping with certain bacterial attacks upon many articles of commerce; for example, they were used to protect casein paints from decomposition and they performed very satisfactorily for such purposes.

The agents of this composition may also be used as additives to many other film-forming compositions and penetrants in addition to their useful role in casein paints. For example, they may be introduced into varnishes, water repellants for textiles and wood, plastics, linoleum, oil paints, polishes, waxes, and a wide variety of other products. They are useful as pest control agents in these compositions and they also have a pronounced protective effect upon the articles of commerce to which these compositions are applied. For example, the use of a water repellant upon a tent fabric may reduce the water permeability of the fabric, but would not protect the fabric from rotting due to fungus growth. The inclusion of the agent of this invention in a water repellant composition would protect the fabric treated from such fungus growth.

The foregoing detailed description sets forth the invention in its preferred practical form, but the invention is to be understood as fully commensurate with the appended claims.

Having thus fully described the invention, what I claim as new and desire to secure by Letters Patent is:

1. A substantially water-insoluble and substantially benzine-soluble alkyl dimethyl benzyl ammonium naphthenate wherein the alkyl group contains from 12 to 18 carbon atoms.
2. A substantially water-insoluble and substantially benzine-soluble dodecyl dimethyl benzyl ammonium naphthenate.

MILTON NOWAK.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

| Number    | Name      | Date          |
|-----------|-----------|---------------|
| 2,079,613 | Holt      | May 11, 1937  |
| 2,115,250 | Bruson    | Apr. 26, 1938 |
| 2,137,465 | Thackston | Nov. 22, 1938 |
| 2,176,896 | Epstein   | Oct. 24, 1939 |
| 2,295,504 | Shelton   | Sept. 8, 1942 |
| 2,295,505 | Shelton   | Sept. 8, 1942 |
| 2,302,805 | Schussler | Nov. 24, 1942 |

#### OTHER REFERENCES

- Alkaline Earth and Heavy Metal Soaps by Elliott, pages 144-147 and 171.